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FEBRUARY, 1928

Notes on the Geographical
Paramagnetism in Liquid Nitrogen
Scattering and Polarization
of
Production of Atomic
Compton Effect in
Reflection in the
of a Luminescent
Band of Positive Ions
Measurement in
Thermionic
between the
of Single
Diffusion
on the
Scattering
Absorption of
Phenomena

Second Series *February, 1928* *Vol. 31, No. 2*

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PHYSICAL REVIEW

HIGH ALTITUDE TESTS ON THE GEOGRAPHICAL, DIRECTIONAL, AND SPECTRAL DISTRIBUTION OF COSMIC RAYS

By R. A. Millikan and G. H. Cameron

Abstract

Intensity of cosmic rays in the high Andes.—Depth-ionization readings taken in Lake Miguilla, Bolivia (alt. 4570 m) and on Lake Titicaca (3820 m) agreed closely with observations in the northern hemisphere previously reported.

Intensity of cosmic rays at sea-level.—Three electroscopes which differed considerably in form, wall material and volume, all agreed in giving at sea-level an ionization of 1.4 ions/cc/sec.

Effect of Milky Way on cosmic ray intensity.—Two sets of day and night observations, each of three days duration, in a deep valley of the Andes at 4700 m elevation failed to bring to light any difference between the radiation coming in from the plane of the Milky Way and the plane normal thereto.

Spectral distribution of the cosmic rays.—A new curve which includes the readings in South America and those published in 1926, analyzed by the method before used, yields absorption coefficients which vary from $\mu=0.25$ per meter of water to $\mu=0.15$. The corresponding wave-lengths, using the Compton equation, are .000525A and .00032A.

Ionization at extreme altitudes.—Under the assumption that the largest absorption coefficient, viz. $\mu=0.25$, is valid for the upper regions of the atmosphere, the ionization at any altitude may be calculated, with the aid of the Gold tables, taking the sea-level value as 1.4 I/cc/sec. The total ionization, computed from this data by a graphical integration, for the Millikan and Bowen sounding-balloon observations reported in 1926, shows remarkable agreement with their experimental result. This implies that the wave-lengths of the rays entering the atmosphere are not appreciably different from those at altitudes at which we have ourselves taken observations.

Effects of thunder-storms on cosmic rays.—Lake Miguilla, Bolivia, is completely screened from thunder-storm influences and yielded the same value of the cosmic rays as regions not so screened. Also sea-level observations taken in the midst of heavy thunder-storms showed no influence of these on cosmic ray readings.

I. Introductory

THE experiments reported herewith were performed in the High Andes of Bolivia, and on the ocean voyage thereto in the summer of 1926. They had four principal objectives.

The first was to see whether in high altitude lakes in the southern hemisphere the altitude-ionization curve would coincide with that found in lakes

in the northern hemisphere. This curve was particularly sensitive in the very high altitude lakes obtainable in the High Andes and the spectral distribution found in 1925 could be more accurately tested. If the northern hemisphere and the southern hemisphere curves coincided it would go a long way toward eliminating the possibility that the rays are generated by the incidence of high-speed beta-rays on the very outer layers of our atmosphere—about the only hypothesis which could put the source of these rays in the last tenth of the air above the earth—the approximate height reached in Millikan and Bowen's high-altitude sounding-balloon work (see below). For such beta-rays would be expected to be influenced by the earth's magnetic field so as to generate stronger radiation over the poles than over the equator. In latitude 17, south, we should be completely screened from such pole effects, particularly if we could get into suitable high-altitude pockets in the mountains.

The second was to obtain further crucial tests of the C. T. R. Wilson hypothesis that these rays may be due to the integration of the effects of the impact in the earth's atmosphere of electrons endowed with many millions of volts of energy acquired in thunder-storms. Lakes in suitable pockets in the High Andes would be completely screened from such effects. Also a comparison of the rays found in thunder storm areas with those found in large regions, like California, which are comparatively free from thunder-storms, might furnish check observations upon this point.

The third was by determining through deep under-water observations the zero readings of new electroscopes, to obtain new checks on our value of the ionization due to the cosmic rays at sea-level, a quantity for which as yet there have been wide divergences between the results of different experimenters.[1]

The fourth was to get into suitable pockets or valleys in very high mountains where the rays are three or four times as intense as at sea-level, and there to make more reliable tests on directional effects in cosmic rays—in particular to see whether the Milky Way is more or less effective than other portions of the sky in sending these rays into the earth.

II. Geographical Distribution

The South American lake chosen as most suitable for the under-water readings was Lake Miguilla near Caracoles, Bolivia. This is a snow-fed lake 125 feet deep lying at an altitude of 15,000 feet (4570 meters), 3200 feet higher than Muir Lake, in which our highest under-water readings in the northern hemisphere had been taken. It was perhaps 700 feet in width and 2000 feet in length, and surrounded on all sides by mountains, the angular elevation of which as seen from our raft anchored in the middle was about 17 degrees. The cosmic rays coming in at an angle less than this to the surface are so fully absorbed by their long path through air that their total contribution to the cosmic rays coming in from the hemisphere

[1] Swann, Phys. Rev. **29**, 372 (1927), finds the ionization due to them on the summit of Pike's Peak 0.75 per cc per sec. per atmosphere, while we found them in the same place to be close to 5 ions.

above is negligible. The lake, on the other hand, was completely screened by the mountains from the hypothetical rays generated in thunder-storms. The zero readings of the two electroscopes used, *i.e.*, the readings corresponding to depths of immersion of more than 20 meters, were 6.8 for electroscope number 1, and 2.4 for electroscope number 4. Of course the readings of significance for our purpose were those taken near the upper part of the depth-ionization curve. The differences between the foregoing zeros and the readings at depths corresponding to the upper part of the curve are given in Table I. Accidents to the electroscopes after these readings were taken prevented the lower part of the curve from being as accurately filled in, but this was of no importance since this portion could be studied much more accurately in lakes nearer home.

TABLE I

Ionization readings at various depths in Lake Miguilla. The values are expressed in ions per cc per sec.

Depth beneath surface	0	1/2 m.	1 m.	3 m.	5 m.
Electroscope No. 1 (1st run)	7.74	5.26	4.04	1.8	1.14
Electroscope No. 1 (2nd run)			4.1		1.15
Electroscope No. 4			4.14		1.14
Means	7.74	5.26	4.09	1.8	1.14

We have plotted these readings taken in South America on the same sheet with those taken with electroscope No. 1 in 1925 in Muir Lake and in Arrowhead Lake in California,[2] adding the new cosmic ray readings to the old zero, 7.4, instead of to the new zero, 6.8, and have then drawn a smooth curve to fit as nearly as possible the whole set of points taken from both hemispheres. Fig. 1 shows this curve. It furnishes the best of evidence that the cosmic rays are quite independent of geographical position, the points taken in the southern hemisphere fitting this one curve quite as well as do the points taken in the northern hemisphere. The two points that fall farthest from the curve correspond to single readings, and hence should be given little weight in comparison with points which represent the means of three or four readings.

The reading at the surface, viz. 7.74, not indicated in Fig. 1, falls about two ions above the curve, as it should do in conformity with the Muir Lake work, because of the presence at the surface of local radiations from the mountains and the atmosphere. In conformity, too, with the findings at Muir Lake the reading 5.26 at 1/2 meter is slightly above the curve, since this thickness of water is insufficient for the complete absorption of these softer rays from the mountains and the atmosphere. From the absorption coefficient of the hardest of the radioactive radiations it is easy to compute that no such rays can affect the reading at one meter depth. In this work, too, the three different observations taken at one meter are so consistent that this point may be taken as fixing the curve with considerable certainty at this elevation. The readings at five meters are seen to be equally con-

[2] Millikan and Cameron, Phys. Rev. **28**, 851 (1926).

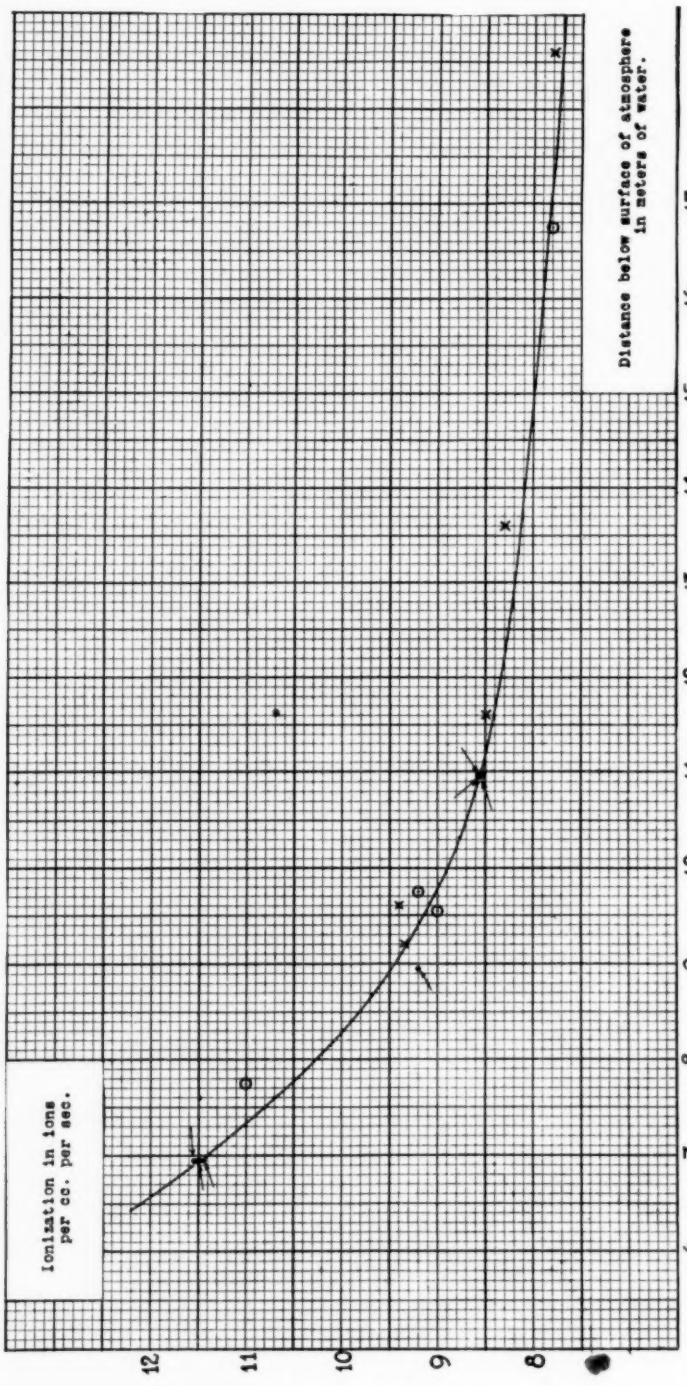

Fig. 1. Ionization due to cosmic rays at various depths in meters below the surface of the atmosphere. Dots represent readings at Lake Miguilla, Bolivia; crosses in Lake Arrowhead, California; circles in Muir Lake, California.

cordant. The present curve is then the best we have yet presented for studying spectral distribution. (See section V.)

We also took a series of readings on the surface of Lake Titicaca (altitude 12,500 feet, 3820 meters) and found there the mean reading 12.3 ions in electroscope No. 1. It is interesting to compare this result with very careful and very complete sets of readings on shipboard taken all the way from Los Angeles to Mollendo, Peru. The mean of a very large number of consistent readings taken in this way with electroscope No. 1 was 8.29. The difference between these readings at sea and those taken in just the same way on Lake Titicaca is $12.32-8.29=4.03$. The increase in cosmic rays shown by the curve between sea-level and 12,500 feet is $12.0-8.8=3.2$. The excess of 0.8 ions per cc. per sec. is easily accounted for by the proximity of mountains bordering Titicaca, for these are very low-lying and should have added a little, but only a little, to the surface reading. So that the Titicaca readings speak, though in a less precisely quantitative way than the curve, for the uniformity of the cosmic rays the world over at a given height.

Further, if we take the difference between the zero reading of electroscope No. 1 and the reading on Lake Titicaca we obtain $12.32-6.8=5.52$. Now, the cosmic ray ionization shown at 12,500 feet by our original cosmic ray curve for electroscope No. 1 was $12.3-7.4=4.9$, and the cosmic ray ionization at 12,500 taken from the new cosmic ray curve is $12.0-7.4=4.6$. The two curves are then at this point in fairly close agreement and together they yield an ionization at 12,500 0.77 ions lower than that observed on the surface of Lake Titicaca, in close agreement with the 0.8 ions excess obtained above, so that from every angle from which we can approach it from our data the surface reading at Lake Titicaca is about 0.8 ions above the value of the cosmic rays alone at that elevation. From the old curve, from the new curve, and from the Titicaca surface readings, then, the conclusion that the cosmic ray ionization at 12,500 is not far from 4.6 ions is unavoidable.*

Sea-level observations taken in the midst of powerful thunder-storms showed no influence of these storms upon the electroscope readings.

III. Sea-Level Cosmic Ray Ionization

The value of the sea-level cosmic ray ionization which we have heretofore published from our 1925 observations with electroscope No. 1 was 1.4 ions per cc per second. This value can be obtained directly by reading off the ordinate at 10.33 meters of the former cosmic ray curves for electroscope No. 1 and subtracting the zero value, viz., 7.4. The same procedure applied to the cosmic ray curve for electroscope No. 3 gives, however, 1.6 ions per cc per second. Whether the discrepancy was due to different effects of electroscope walls or to imperfections in the determination of electroscope capacities, we were in 1925 uncertain. Electroscope No. 3 suffered an accident which made a redetermination of its capacity impossible, but electroscope No. 1, used again in this work, and the new electroscope No. 4, identical in con-

* Swann's conclusion that the ionization due to cosmic rays on Pike's Peak is less than 1 ion is quite irreconcilable with all three of these findings.

struction with No. 3, had their capacities measured carefully at the initiation of the present work. When placed side by side and subjected to the same change in radiation, they showed, within the limits of observational error, the same change in ionization, thus indicating that though No. 1 had a volume of 1890 cc and a wall thickness about 2 mm, while No. 4 had a volume of 3210 cc and a wall thickness of 3 mm, yet these wall and volume differences had no appreciable effect on the indicated ionization per cc. This fact is brought sharply to light in Table II, in which the maximum divergence from the mean value of I/cc/sec is under three percent, which is quite as close as our claims for precision can be in these particular readings.

TABLE II

Equality of the ionization in two electroscopes of different walls and volumes.

Place of observation	No. 1 I	No. 4 I	Mean I
Side by side readings, Pasadena Institute campus	12.36	8.54	
Side by side readings in small boat Balboa Harbor	8.79	4.78	
Total differences in incoming radiation	3.57	3.76	3.66
Side by side readings, Caracoles mountain side	20.42	16.03	
Side by side readings, Titicaca Lake surface	12.32	7.86	
Total differences in incoming radiation	8.10	8.17	8.13
Side by side readings, Lake Miguilla, 1 m. immersion	10.9	6.54	
Side by side readings, Lake Miguilla, 5 m. immersion	7.94	3.50	
Total differences in incoming radiation	2.96	3.04	3.00

In the new composite curve, Fig. 1, involving readings in both hemispheres, the ionizations in Lake Miguilla given by both electroscopes No. 1 and No. 4, after the subtraction of their zero readings and the addition of the differences to the old zero 7.4, are included, so that the new curve has a greater generality, not only as to lack of dependence upon geographical position, but also as to freedom from instrumental peculiarities than any we have thus far presented.

It will be seen, however, that the sea-level value of the cosmic rays as read from the new curve is exactly 1.4, the same we have heretofore published for electroscope No. 1 alone. Further, we have very recently built a new steel electroscope of highly increased sensitivity and have found that although its shape, wall material and volume are different from the corresponding elements in No. 1 and No. 4, yet the sea-level ionization yielded by it in an exceedingly satisfactory series of depth-ionization readings (to be presented in a subsequent article) is again 1.4 with, however, an absolute uncertainty not yet accurately determined. *We shall therefore fix upon 1.4 as the value of the cosmic ray ionization at sea-level within an ordinary electroscope.* This value may need slight modification to conform to the peculiarities of individual electroscopes, but the foregoing agreements in the case of three different electroscopes indicate that, for rays as hard as the cosmic rays, such influences will be but slight. We shall present a later report upon the effect of walls.

IV. Tests on the Influence of the Milky Way on Cosmic Ray Intensities

The position of the sun having been shown by all observers to have no influence whatever upon the intensity of the cosmic rays, the next important step of the same kind is obviously to make as careful tests as possible upon the effect of the Milky Way. Up to the time at which the following experiments were performed Kolhörster[3] had obtained indications at an altitude of 3550 meters of something like a 15 percent increase in the cosmic radiations coincident with the culmination of the Milky Way, although he could bring to light no such effect at sea-level.

Since unambiguous evidence upon this point would have the most important bearing upon the source of the cosmic rays, we sought a valley at the highest obtainable altitude where the surrounding mountains would cut off entirely any possible influences from the Milky Way during a period of at least four or five consecutive hours. We found such a situation at the mining camp of the Caracoles Tin Company, altitude 15,400 feet, an elevation at which according to the curve of Fig. 1 the ionization due to cosmic rays has the very considerable value of 5.5 ions. On account of the shielding effect of the mountains this value was reduced at the point of observation

Table III

Observations on directional effects on cosmic rays.

1st Series 3 days duration			2nd Series 3 days duration		
4:22 P. M.– 6:17 P. M.	16.4	min.	9:19 P. M.– 2:17 A. M.	12.87	max.
6:47 P. M.–10:25 P. M.	16.3	max.	2:40 A. M.– 7:30 P. M.	12.83	min.
8:55 A. M.–11:14 A. M.	15.8	max.	7:55 A. M.– 1:05 P. M.	12:92	max.
11:51 A. M.– 3:15 P. M.	16.1	max.	1:47 P. M.– 6:44 P. M.	12.80	min.
3:49 P. M.– 8:28 P. M.	15.8	max.	6:58 P. M.–11:20 P. M.	12.97	max.
8:44 P. M.–11:01 P. M.	15.95	max.	1:39 A. M.– 7:43 A. M.	12.90	min.
8:52 A. M.–11:05 A. M.	15.7	max.	8:10 P. M.– 1:12 A. M.	13.02	max.
11:19 A. M.– 1:46 P. M.	15.75	max.	2:13 P. M.– 6:45 A. M.	13.08	min.
2:10 P. M.– 4:39 P. M.	16.1	min.	6:57 P. M.–10:16 P. M.	13.08	max.
5:19 P. M.– 6:56 P. M.	16.4	min.			
Mean =	16.03		Mean =	12.94	
Mean max = 15.93; mean min. = 16.17			Mean max = 12.97; mean min. = 12.90		

to 3.6 ions. The Milky Way was practically out of sight between the hours of 2:30 and 7.

In this position we took two sets of continuous readings, observing night and day for a period of three days in each set. The actual readings are given in Table III. Such accuracy as was obtained is revealed in the consistency of the readings themselves. It will be seen that in the first set the "mean max.", which signifies merely the mean of the observations taken when the Milky Way was in culmination, is a trifle less than the "mean min." (Milky Way out of sight). But in the second set these relations

[3] Kolhörster, Sitz. Ber. d. Preuss. Akad. **34**, 366 (1923).

become inverted. The observational error of the means can scarcely be more than about 0.1 ions, or three percent of the 3.6 ions under observation.

Although the precision and consistency of our electroscope readings still leave much to be desired, we think that a conservative conclusion from these readings is that, if there be any effect whatever of the Milky Way upon the cosmic radiations, the rays coming to us from its direction cannot be six percent greater nor less than are those coming from the portion of the heavens at right angles to the Milky Way. This is in agreement with our preceding less discriminating measurements, and also with recent very careful work at sea-level done subsequently to this by Hoffmann[4] and Steinke,[5] who can find there no directional effect in cosmic rays at all; but it is at variance with results reported by Büttner[6] and by Kolhörster.[7] The present work, however, was probably done under quite as favorable conditions as to altitude and constancy of temperature as have ever been used. It is very important to obtain unambiguous evidence upon this point. No entirely reliable conclusions about the origin of the rays can be drawn until it is settled. As yet the case for a favored region from which the rays come does not seem to have been established, but more sensitive tests can be made and will be made in the near future. *For the purposes, however, of the computations in the next section the foregoing results wholly justify the assumption of a cosmic radiation coming in to the earth equally from all directions and producing an ionization in accordance with the Gold table,*[8] instead of with the usual linear absorption law used by all other observers. The application of the linear absorption law leads to widely different results at high altitudes. Indeed, with the same value of the absorption coefficient, viz. 0.25 per meter of water, and the same value of the sea-level ionization the Gold table gives an ionization of the "top" of the atmosphere of 75 ions per cc per second, while the linear law yields 19 ions per cc per second.

V. Spectral Distribution of Cosmic Rays

From our analysis, with the aid of the Gold table, of our depth-ionization curve from electroscope No. 3 we brought to light sharply in 1926 a definite hardening of the cosmic rays from $\mu = 0.30$ per meter of water at the depth beneath the surface of the atmosphere corresponding to the altitude of Muir Lake, to $\mu = 0.18$ at the bottom of the curve, that is, between say 13 meters and 23 meters beneath the surface of the atmosphere. We commented in our 1926 paper on the fact that electroscope No. 1 gave a slightly lower value of μ for the top of the curve than did electroscope No. 3. The new work with two new electroscopes, viz. No. 4 and the new sensitive one of steel mentioned above, checks the former results with electroscope No. 1 and indicates that the former curve of No. 3 was the less reliable of the two. The new composite curve, Fig. 1, is considerably more reliable than are either

[4] Hoffmann, Ann. d. Physik **80**, 779 (1926).
[5] Steinke, Zeits. f. Physik. **42**, 570 (1927).
[6] Büttner, Zeits. f. Geophys. **2**, 187 (1926); **2**, 291 (1926).
[7] Kolhörster, Naturwiss. **14**, 936 (1926).
[8] Gold, Proc. Roy. Soc. **A82**, 152 (1909).

of the former curves, since it both extends to higher altitudes where the curve is very sensitive, and is a composite of readings with several electroscopes and in widely separated localities.

The upper portion of the new curve, *i.e.*, the portion between the abscissas 6.4 and 9.3 or from about a half meter below the surface of Lake Miguilla to about the same depth beneath the surface of Arrowhead, yields, with the aid of the Gold table, used precisely as in our 1926 paper, the coefficient $\mu = 0.25$. Further, the curve yields the same value of μ whether tested from 6.3 meters to 7.4 meters, or from 7.4 to 8.4, or from 8.4 to 9.4; but from 9.3 to 10.3 (sea-level) the value of μ comes out 0.23. In other words, there is a slight hardening of the rays detectable in the region between Lake Miguilla and sea-level. From 10.3 m to 12.3 m there is still further hardening, the curve yielding the value $\mu = 0.20$ with a discrimination of one point, or at most two points, in the last place. At the lower end of the new composite curve, however, for example between the depths 12 m and 18 m, the coefficient has dropped definitely to a mean value of 0.15, which is also the mean value yielded by the old curve of electroscope No. 1. *The conclusion which we before reached of a spectral distribution of a little less than an octave is reaffirmed by this new work, though the range in μ is now from 0.25 to 0.15 instead of from 0.30 to 0.18.* The corresponding wave-lengths, if computed by A. H. Compton's formula, are 0.000525A and 0.00032A.

VI. The Hardness of the Cosmic Rays Coming into the Top of the Atmosphere and the Ionization Produced in the Atmosphere by Them

Having now fixed upon the value of the ionization at sea-level due to cosmic rays at 1.4 I/cc/sec and the absorption coefficients up to a height of 15,000 feet (4570 meters), we can now, with the aid of the Gold table, compute the precise values of the ionization due to cosmic rays at all altitudes up to this limit with much greater confidence than heretofore.

Further, if the rays which enter the top of the atmosphere are of the same wave-length as those found at an altitude of 15,000 feet we can compute the ionization at all high altitudes. The observations made by Millikan and Bowen[9] with sounding balloons furnish excellent means of testing this hypothesis. Before making the tests it is interesting to point out how large a change of the ionization at high altitudes corresponds to a small change in the value of μ. Thus using the value of μ found in the literature in 1921, viz., 0.57, the ionization at the "top" of the atmosphere (treated as homogeneous) comes out 463 I/cc/sec if the rays are assumed to come in vertically and to produce 1.4 I/cc/sec at sea-level. Lowering the value of μ from 0.57 to 0.25 reduces this "top" value of the ionization to 18.5, *i.e., to about 1/25th of the first mentioned value.* This merely illustrates how sensitive very high altitude flights are for the fixing of mean absorption coefficients. Again, if the rays come in from all directions instead of vertically, high altitude flights show the difference in ionization very easily, for with a value

[9] Millikan and Bowen, Phys. Rev. **27,** 353 (1926).

of $\mu = 0.25$ the Gold table gives an ionization at the "top" of the atmosphere of 75 I/cc/sec in place of the 18.5 I/cc/sec computed for vertical rays.

For the sake, then, of gaining information as to the character of the cosmic rays when they enter the atmosphere, we have computed with the aid of the Gold table the number of ions to be expected at a series of altitudes up to the top on the hypothesis that from 15,000 feet up $\mu = 0.25$. The results from sea-level up, taking for the sea-level ionization 1.4 and for the region 9.3 m to 10.3 m $\mu = 0.23$ and for all altitudes above 9.3 m $\mu = 0.25$, are contained in Table IV.

TABLE IV

Ionization of the atmosphere per cc per sec. by cosmic rays.

Altitude (kilometers)	Distance below top of atmosphere (meters of water)	I	Altitude (kilometers)	Distance below top of atmosphere (meters of water)	I
0	10.33	1.4	11	1.87	25.8
0.9	9.3	1.88	12	1.53	30.3
5	5.3	7.04	13	1.30	33.8
6	4.5	9.58	14	1.11	36.6
7	3.85	11.80	15	.93	40.4
8	3.25	14.81	17.5	.62	48.0
9	2.73	18.20	20	.42	54.1
10	2.25	21.1		0	75.0

In the record of Millikan and Bowen's high altitude flight they give the mean discharge rate, in the ascent from 5 km to 15 km and the descent again to 5 km, as 46.2 I/cc/sec. They also give the discharge rate of the same electroscope at the earth's surface as 15.4 ions. The local radiation plus the cosmic rays at the point in Pasadena where the last reading was taken was 5.4 ions, thus making the zero of this electroscope 10 ions, on the assumption that it would agree with the three tested above in the value of the ionization produced by a given external source. This gives the mean value of the ionization due to cosmic rays during the flight from the 5 km altitude up to the 15 km altitude and back to the 5 km altitude as $46.2 - 10 = 36.2$ I/cc/sec. This multiplied by the total number of seconds of the duration of the flight from 5 km up to 15 km and back to 5 km, namely 8100, gives 29,300,000 as the observed number of ions formed per cc. during this interval. The theoretical number obtained by dividing the time of flight into 15 minute intervals and multiplying the number of seconds in the interval by the value of the ionization at the mean height during the interval (Table IV) is 29,250,000.

The extreme closeness of the numbers is of course accidental, but the agreement shows that the curve of Fig. 1 extended up to the top of the atmosphere with the aid of the coefficient which holds at its upper end, namely, $\mu = 0.25$ strikes exactly our observed point at 15 km altitude, which is 0.91 of the way to the "top." *This fact lends a new significance to Table IV, which now represents, not hypothetical ionizations, but actual ionizations as determined by an experimental cosmic ray curve well filled in from 4570 m*

down, and with one point inserted at the 15 km altitude. From these facts the inference is scarcely avoidable that the cosmic rays represent a spectral region or band which starts quite sharply at $\mu = 0.25$ on the long wave-length side and extends about an octave (possibly more) towards shorter wave-lengths. The reduction of these absorption coefficients to wave-lengths is, of course, uncertain, Dirac's formula being probably the most correct, but for the sake of comparison with our former data we give the corresponding Compton wave-lengths viz; 0.00053 and 0.00032A. Dirac's formula gives thirty percent shorter wave-lengths.

NORMAN BRIDGE LABORATORY OF PHYSICS,
CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA.
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X-RAY DIFFRACTION IN LIQUID NORMAL PARAFFINS

By G. W. Stewart

Abstract

X-ray diffraction as a function of angle in liquid pentane, hexane, heptane, octane, nonane, decane, dodecane, tetradecane and pentadecane.—In the ionization diffraction-angle curve, there was one diffraction peak only, instead of two as found by Stewart, Morrow and Skinner with the primary alcohols and normal fatty acids. The absence in the *n*-paraffins of the second peak, which, in the alcohols and fatty acids, indicated a longitudinal spacing, is explained qualitatively by a consideration of the longitudinal molecular forces. These could not produce as uniform a longitudinal arrangement as occurs in the other compounds. The single peak was located at the same angle with each *n*-paraffin, excepting, at first, pentane and decane. Subsequent purification of the pentane produced no alteration in the peak position but when the sample was finally made synthetically, the peak came into coincidence with that of the other seven. The decane is believed to contain isomers. The lateral separation of molecules is approximately 4.6A and is essentially the same as in the liquids previously studied and referred to in this paper. In six of nine cases, the diffraction intensity does not decrease as one approaches 0°. The significance is not clear though one is reminded of total reflection and also of refraction. If one assumes the *C* atom to occupy a length in the chain of 1.3A, as found by other observers of x-ray diffraction in solids, and the length of H, 1.0A, and if one assumes the volume occupied by a molecule to be the square of the lateral spacing times the molecular length, then the computed values of densities of the seven normal paraffins are correct to within less than 4 percent or a mean of 2 percent. Two additional but faint peaks in the diffraction intensity curves are found with pentadecane and tetradecane. The corresponding spacings are 2.1A and 1.23A. The nearness of these to the repetitive values of 2.0A and 1.26A which are found in a diamond, is suggestive.

THIS is a continuation of the studies of Stewart and Morrow,[1] Stewart and Skinner,[2] and R. W. Morrow[3] wherein the molecular space arrangement has been shown to be significant in liquid primary normal alcohols, a few of their isomers and liquid fatty normal acids. As will be shown, the present results upon liquid *n*-paraffins are in harmony with the view that the molocules are oriented, and that the separation of the molocules in a direction perpendicular to their lengths is the same as in primary normal alcohols and in fatty acids.

Pentane, hexane, octane and decane were obtained from the Research Laboratory of the Eastman Kodak Company. Heptane, nonane, dodecane, tetradecane and pentadecane were made especially for us by the Northwestern Public Health Institute, through the kindness of Professor F. C. Whitmore.

[1] Stewart and Morrow, Phys. Rev. **30,** 232 (1927).
[2] Stewart and Skinner, Phys. Rev. **31,** p. 1 (1928).
[3] R. W. Morrow, Phys. Rev. **31,** p. 10 (1928).

Apparatus, method and results. The apparatus and method are essentially the same as that previously described. In Fig. 1, are shown the diffraction curves of normal pentane, hexane, heptane, octane, nonane, decane, dodecane, tetradecane and pectadecane.

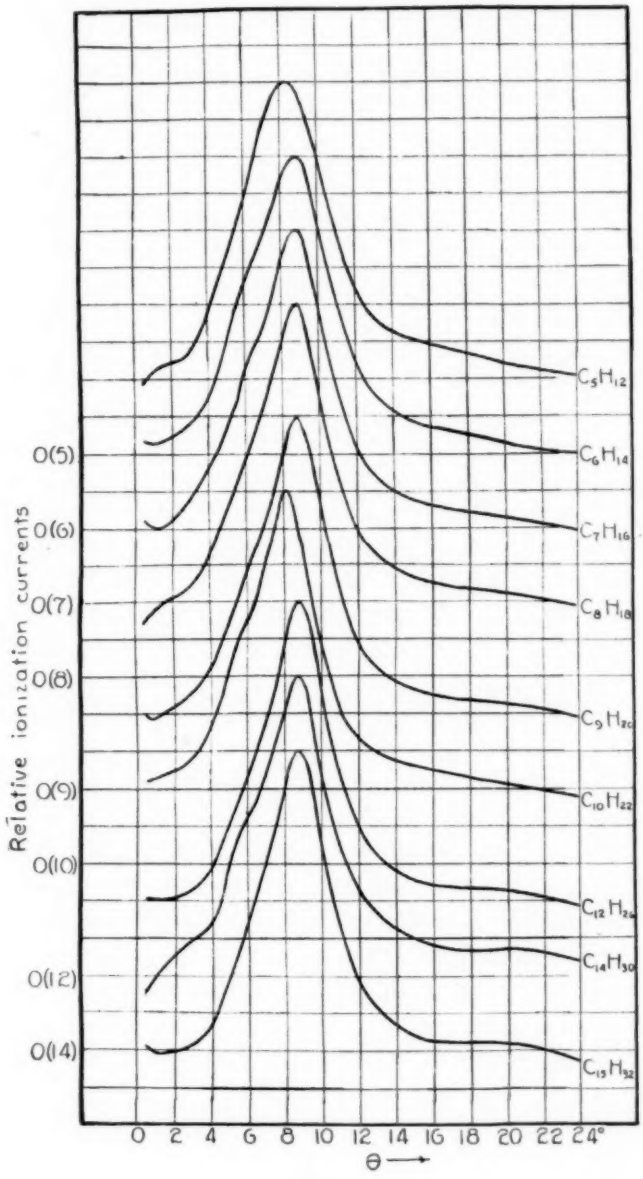


Fig. 1

Discussion of results. The chief feature of the curves in Fig. 1, as compared with those obtained for the primary normal alcohols and the normal

fatty acids, is the existence of but one peak. The positions of the two peaks in these other compounds were interpreted as caused by the spacing between the molecules lying in a parallel collinear arrangement, and by the length of the molecule, or, rather, by the length of two molecules in series having attached polar groups. The latter peak indicated the much lesser intensity of diffraction. It is not surprising that in the case of the normal paraffins, with the electron content more uniformly distributed, this peak of feeble intensity was not found. The reason that the intensity with the primary *n*-alcohols and normal fatty acids is small, may be found in the difference in the uniformity of the arrangement longitudinally and transversely and in the concentration of electrons. The molecular binding forces that determine the side by side array may be greater, or they may be more effective in producing uniform parallel spacing because of the length of the chain over which the forces act. The side spacing would be in evidence, even though the ends (or centers) of the adjacent molecules did not lie approximately in a plane. On the other hand, the longitudinal spacing might be regular in any one of the successive parallel chains, but yet without the termini of the molecules lying in transverse approximate planes. In short, there may easily be longitudinal slippage with the diffraction intensity determined by the degree of the definiteness of these transverse planes. Obviously, the primary *n*-alcohols and *n*-fatty acids, with the OH and COOH groups, would, on account of the mass concentration, have greater longitudinal uniformity of arrangement among the parallel chains. Thus, the absence of the second peak with *n*-paraffins rather emphasizes the correctness of the former interpretation of the two peaks. It accentuates the interpretation that we are dealing with a space arrangement giving x-ray diffraction effects that should be interpreted as caused by something more than merely averaged distances between molecules.

The point of greatest quantitative interest is the fact that the single peak has a maximum at little more than 8.8° (averaging 8.83°), in all excepting two cases. In accord with Bragg's Law using a wave-length of 0.712A, 8.83° indicates a spacing of 4.63A. This is, within error of observation, the same as with the similar chains in the primary *n*-alcohols and the normal fatty acids. As previously interpreted, this represents the separation of the molecules in a direction normal to their lengths. With the paraffins the separation remains constant although the molecular length is doubled. This justifies the previous interpretations and shows that a wholly random orientation of molecules does not occur.

It is noticed that the maxima with pentane and decane are at a distinctly less angle. The research laboratory of the Eastman Kodak Company kindly further purified the pentane but the position of the peak persisted with the new sample. The interpretation at present is that the presence of isomers of heptane and decane cause these displaced angles. This explanation

is reasonable in the light of the experiments on the primary *n*-alcohol isomers. This point should be settled by additional investigation with purer liquids.[4]

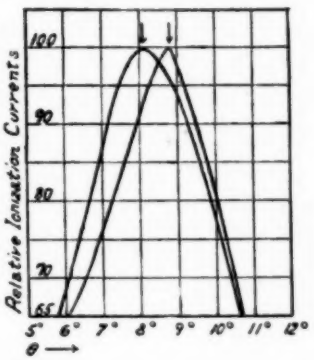
The third point is the evidence in six of the nine curves that the radiation is not approaching zero at 0° for there is noticeably increased scattering as the angle of diffraction becomes less than 1°. While the observations have not been carried to the extent that the quantitative differences between the *n*-paraffins at this small angle are certain, nevertheless there is no doubt but that there is a definite difference at small angles between the *n*-paraffins and the *n*-alcohols. This same effect has been found by Sogani[5] with liquid pentane, hexane heptane and octane but not with cyclo-hexane. He does not comment upon this fact although it is shown clearly in his photographs. One is inclined to think at once of the explanation as similar to that of total reflection at almost glancing angles or of refraction. But it is not clear why this phenomenon appears only in some and not in all of the paraffins.

Müller and Saville[6] studied the solid *n*-hydrocarbons having 17, 18, 19, 20, 21, 22, 24, 27, 31 and 35 carbons. They reached the conclusion that these solids were crystalline and of two stable forms, and that the increase of length of the chain molecule per additional CH_2 is 1.3A. Piper, Brown and Dyment[7] in an investigation of solid hydrocarbons in paraffin wax, with carbon content believed to be from 22 to 34 atoms, found the long spacings such that there is an increase of 1.22A for each CH_2 added to the chain. If we take the approximate value of 1.3A, assume the diameter of the H atom to be 1.0A and compute the densities as if the chains were parallel, normal to the long spacing planes, and in cross section occupying corners of squares, density values very near to the correct ones were obtained. The density is computed to be,

$$\rho = \frac{(\text{Molecular weight} \times \text{mass of } H)}{(4.63)^2 \times \text{length of chain}}$$

The values found for all excepting pentane[8] and decane are 0.683, 0.694, 0.713, 0.722, 0.747, 0.761, and 0.765. The corresponding values given by the International Critical Tables are 0.66, 0.707, 0.718, 0.768, 0.765 and 0.772.

[4] Since submitting the manuscript for this article, the research laboratory of the Eastman Kodak Company has supplied the writer with a sample of synthetic *n*-pentane. It was made from propyl and ethyl iodides. This third sample when compared with the second shows, as illustrated in the accompanying drawing, that the peak now appears at 8.8°, instead of 8.1°, and that it has become much narrower. This relatively large change in θ is both interesting and suggestive. The peak for *n*-pentane, made synthetically, now coincides with the other seven, leaving additional tests upon *n*-decane for the future.



[5] Sogani, Indian Jour. of Phys. **1**, 237 (1927).

[6] Müller and Saville, Jl. Chem. Soc. **27**, 599 (1925).

[7] Piper, Brown and Dyment, Chem. Soc. Jl., **127**, p. 2194 (1925).

[8] The computed density of the *n*-pentane mentioned in footnote 4 is found to be 0.66, within 4 percent.

The maximum difference between the computed and the correct values is less than 4 percent and the mean difference is less than 2 percent. The agreement may be regarded as an interesting consistency between the arrangement in a liquid and that found in the solid.

Diffraction curves were taken from 0° to 50° with pentadecane and tetradecane. An unmistakable maximum occurred at 19.4° and 19.0° respectively. The peak was only about 10 percent of the total height of the curve. With lauryl alcohol[1] there was a small peak at 19°. Apparently in none of these curves can the additional peak be merely one of a higher order. In the cases of pentadecane and tetradecane there is also a second additional peak at about 33.5°. The two spacings corresponding to 19.4° and 33.5° are 2.1 and 1.23A respectively. As pointed out by Müller and Shearer[9] linkages of carbon atoms can be found in the diamond, with distances of separation projected on a median line of both 1.26A for single and 2.0A for certain pairs of atoms. The inference from the earlier part of this paper is that the 1.23A spacing arises in the distance of separation of the carbon atoms along the chain. Perhaps the 2.1A spacing has a significance suggested by the crystal. However, these interpretations are merely tentative. With triethyl carbinol[2] there was found a corresponding peak at approximately 20° and this was interpreted as the third order peak.

There are several recent reports which have a definite bearing upon the material of the present paper. J. A. Prins[10] has recently investigated certain liquid surfaces and has obtained a band of 5.0A for liquid *n*-octane. This is somewhat larger than our value of 4.63A which is undoubtedly caused by the volume and not the surface. An investigation of the crystal structure of *n*-pentane, *n*-hexane, *n*-octane has recently appeared by McLennan and Plummer.[11] They show that at liquid air temperature these compounds show either the monoclinic or the orthorhombic modification. For the latter he finds that the spacing caused by the "diameter" of the molecules, or the length of CH_2, is a little more than 4.3A which is much less than our value of 4.6A. He is also led to believe that the carbon chain is straight, which is not in accord with the view that appears in the work of other investigators[12] of compounds in solid form having similar chains. Neither is it in harmony with the work of this laboratory in liquids. But in the monoclinic form McLennan and Plummer find a "medium strong" line at 4.61A. On the whole the crystal results would indicate that our liquid space array is more similar to the monoclinic than to the orthohombic modification. From our previous papers it is clear that the liquid space array or the cybotactic state is not like any crystal modification.

[9] Müller and Shearer, Jl. Chem. Soc. **123,** 3156 (1925).

[10] Prins, Physika **6,** 315 (1926).

[11] J. C. McLennan and W. G. Plummer, Trans. Roy. Soc. of Canada **21,** 99 (1927).

[12] Trillat; Piper Brown and Dement; Müller and Saville; Shearer; Saville and Shearer; references to whose articles have been given in the other papers of Stewart and Morrow, R. W. Morrow, and Stewart and Skinner, loc. cit.

J. R. Katz[13] has recently published the results of x-ray diffraction measurements for a large number of liquids including some *n*-alcohols, and their isomers, monobasic acids and *n*-paraffins. His experimental results are in harmony with ours so far as the angle of maximum intensity of diffraction is concerned. But Katz did not find the second inner significant peak which is of prime importance. His report shows that Keesom's formula, wherein the distance is determined by Bragg's law and division by 0.814, does not give molecular mean distances with long molecules. The difficulties that confront Katz in the application of Keesom's formula seem to be removed by the view point of the series of papers from the laboratory of the author. A discussion of this matter can be undertaken to greater advantage in a separate paper.

I am especially indebted to Dr. F. C. Whitmore of Northwestern University for the preparation of the chemicals specified and to Mr. W. D. Crozier, research assistant, for his valuable aid in obtaining the data.

PHYSICS LABORATORY,
STATE UNIVERSITY OF IOWA.

[13] J. R. Katz, Zeits. f. Physik **45**, 97 (1927).

HYPERFINE STRUCTURE AND POLARIZATION OF $1^1S_0-2^3P_1$ OF MERCURY IN RESONANCE RADIATION†

By A. Ellett and Walter A. MacNair*

Abstract

The incomplete polarization of λ2537A of mercury in resonance radiation is due to the peculiar behavior of the outer two hyperfine structure lines. The three remaining hyperfine structure lines behave in accordance with the predictions of the theory of the anomalous Zeeman effect for a $1^1S_0-2^3P_1$ line. Von Keussler's observation of complete polarization in 7900 gausses is explained, in part at least, by the observed shift of the −25.6 hyperfine structure line, and complete polarization is obtained with a field of only 2000 gausses using a resonance radiation source.

THE explanation of the behavior of resonance radiation in strong magnetic fields based upon the quantum theory of the anomalous Zeeman effect has sufficed for a qualitative description of the observed phenomena and has given values for the polarization which agree quite well with experimental results. However, there are certain outstanding discrepancies such as the 80 percent polarization of the 2537A resonance radiation of mercury. Wood and Ellett[1] showed that this resonance radiation when excited by plane polarized light with its electric vibration parallel to the magnetic field in which the resonating vapor was placed was not completely polarized, and that this incomplete polarization was not due to secondary resonance radiation nor to collisions. More recently von Keussler[2] and Olson[3] have shown that the maximum value of the polarization is 80 percent, except in quite intense fields. Von Keussler,[4] using a field of 7900 gausses, was able to obtain practically complete polarization. Olson,[3] von Keussler[4] and MacNair[5] have all suggested that the explanation of the incomplete polarization is to be found in some pecularity of the Zeeman effect of the hyperfine structure. Indeed MacNair[5] has shown that the parallel Zeeman component of the −25.6 milliangstrom unit (M.A.U.) hyperfine structure line shifts toward longer wave-lengths with increasing magnetic fields and he has suggested that this shift may explain the complete polarization found by von Keussler. In a field of 7900 gausses this line is shifted 7.8 M.A.U. and so should not coincide with any emission line of the arc used for excitation. If instead of an arc, a resonance lamp, giving much narrower emission

* National Research Fellow.

† A preliminary note signed MacNair and Ellett appeared in the Proc. Nat. Acad. **13**, No. 8, Aug. 1927. The change in order of the author's names is intended to emphasize the fact that the authors wish to assume equal and joint responsibility.

[1] Wood and Ellett, Phys. Rev. **24**, 243 (1924).

[2] von Keussler, Phys. Zeits. **27**, 313 (1926).

[3] Olson, Phys. Rev. **29**, 207, abstract (1927).

[4] von Keussler, Ann. d. Physik **82**, No. 6 (1927).

[5] MacNair, Proc. Nat. Acad. **13**, 430 (1927).

lines, were to be used as a source it is to be expected that a smaller shift would effect the same result.

With this possibility in view the following experiment was undertaken. The water cooled quartz arcs A and A' (Fig. 1) were used to excite intense resonance in the quartz bulb B, which served as a source for the excitation of resonance radiation in the resonance lamp C. Both B and C were highly evacuated clear fused quartz cells to which were attached side tubes containing a few drops of mercury. The side tube attached to the resonance source B was kept at a temperature of 18° to 20°C, that attached to C at -18°C. A quartz lens and Nicol prism projected a beam of polarized resonance radiation across the resonance lamp C and the path of this beam was photographed by means of the quartz lens and Wollaston prism at D. The Wollaston prism was so oriented that the two images which it pro-

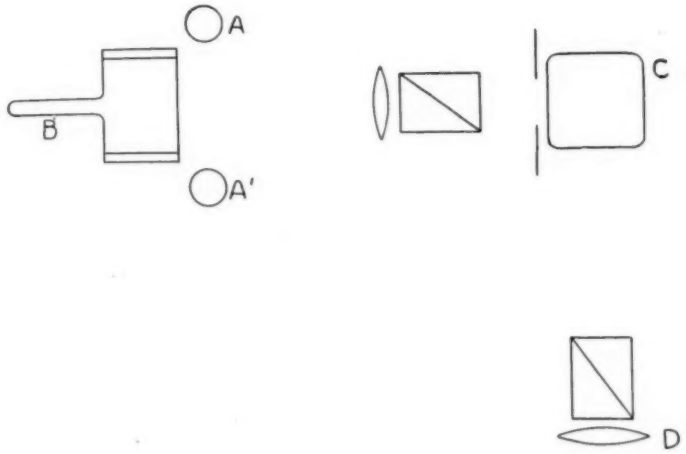


Fig. 1. Excitation of resonance radiation with resonance lamp source

duced contained light polarized respectively parallel and perpendicular to the magnetic field in which the resonance lamp was placed. This field was produced by a Helmholtz coil consisting of 126 turns of copper tubing wound on a mean radius of 10 cms. Water was circulated through the tubing for cooling. The coil was energized by current from a 40 volt 600 ampere generator which made possible a maximum field of 3450 gausses. Surrounding this coil was another Helmholtz coil of 50 cms radius used to compensate the earth's magnetic field for such observations as were made in zero field.

Results

In zero field resonance radiation excited by plane polarized *resonance radiation* is about 80 percent plane polarized. In a magnetic field parallel

to the electric vector of the plane polarized exciting beam the polarization increases with increase of magnetic field and becomes sensibly complete in a field of 2000 gausses. This statement is based on the fact that the weaker of the two images produced by the Wollaston prism D attained considerable density* with exposures of one minute in zero magnetic field, whereas no trace of it was apparent with exposures of 20 minutes in a field of 2000 gausses. The total intensity of the resonance radiation is somewhat less in 2000 gausses than in zero field, but the decrease does not exceed 25 percent.

Discussion

R. W. Wood,[6] who was the first to obtain the true hyperfine structure of λ2537 showed that the line consists of five hyperfine structure lines spaced about −24, −10, 0+11 and +22 M.A.U. He also showed that the results of Nagaoki and others were due to self reversal in the source. Wood made a few observations on the Zeeman effect of the hyperfine structure lines but reached no definite conclusion.

The hyperfine structure and Zeeman effect has since been studied by MacNair who has shown that the spacing of the five components is −25.6, −10.3, 0.00, +11.6, and +22.1 M.A.U., and as was mentioned above, he has also found that the parallel Zeeman component of the −25.6 M.A.U. line shifts toward longer wave-lengths with increase of magnetic field. The shift is given by the equation $\Delta\lambda = 0.089\ (H)^{1/2}$.

In a field of 2000 gausses this amounts to 4.0 M.A.U. The Doppler breadth of any component line of 2537 at 18°C is 2.6 M.A.U. and if the breadth of the fine structure lines does not much exceed this it is evident that a shift of 4 M.A.U. will reduce the absorption of the −25.6 component to a negligible amount. As a result of this experiment it seems reasonable to suppose that the low polarization shown by λ2537 is due to the peculiar Zeeman effect of the −25.6 M.A.U. hyperfine structure line. In order to be certain whether this is the explanation it is necessary to investigate the fine structure of the resonance radiation.

Hyperfine Structure of Resonance Radiation

To excite the resonance radiation two vertical Cooper Hewitt quartz mercury lamps were operated from a 220 volt D.C. line and connected in series with each other and with a large inductance and suitable resistance to keep the current at three and one-half amperes. The arcs were cooled by running water and were placed in a magnetic field of 30 gausses so oriented as to force the discharge against the side of the arc toward the resonance bulb. The light from the arcs was focussed upon the resonance bulb by quartz lenses and polarized in the desired azimuth by Wollaston prisms arranged as shown in Fig. 2. Under these conditions intense resonance radiation was excited in the quartz resonance bulb.

* Density such that from one-half to one-quarter of the incident light was transmitted.

[6] R. W. Wood, Phil. Mag. **50**, 761 (1925).

Since we wished to use only a one centimeter strip of the quartz lens which focussed the resonance radiation onto the Lummer-Gehrcke plate we chose an area that was especially free from strain so that its depolarizing influence was entirely negligible. The Wollaston prism in front of the Lummer-Gehrcke plate divided the incident beam of resonance radiation into two beams one with its electric vector horizontal and the other vertical, so that the interference pattern due to each appeared on the photographic plate separated from that due to the other. The fringe systems were brought to a focus

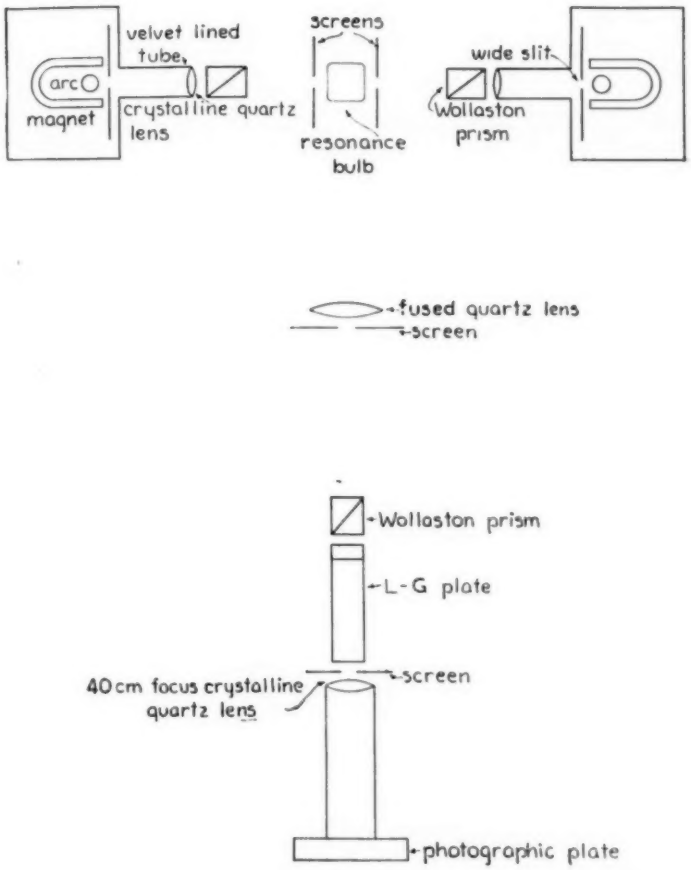


Fig. 2. Arrangement of apparatus for obtaining hyperfine structure of resonance radiation.

upon the photographic plate by a crystalline quartz lens of forty centimeters focus, especially corrected for spherical aberration at 2537A. Stray light was prevented from reaching the photographic plate by taking several precautions, such as placing the arcs in ventilated light-tight boxes, enclosing parts of the light-path in velvet lined tubes, etc.

[7] All three plates were made by Adams Hilger Ltd. A note delivered with the 4.92 m/m plate stated that it gave "specially good definition."

Each of three quartz Lummer-Gehrcke plates[7] was used to obtain the hyperfine structure of the polarized resonance radiation. The following table gives data relative to each. $\delta\lambda_{max}$ is the separation of adjacent orders.[8]

TABLE I

Data relative to the Lummer-Gehrcke Plates.

Thickness of plate (mm)	$\delta\lambda_{max}$ in milliangstroms for λ2537 Extraordinary ray (E horizontal)	Ordinary ray (E vertical)
4.24	52.3	52.8
4.92	45.1	45.5
6.42	34.5	34.8

Since the hyperfine structure of the resonance line of mercury is well known we may set down the patterns to be expected from each plate as follows (Fig. 3). The diagram is for the electric vector vertical. If it were taken horizontal the separations of fringes of overlapped orders would be slightly different.

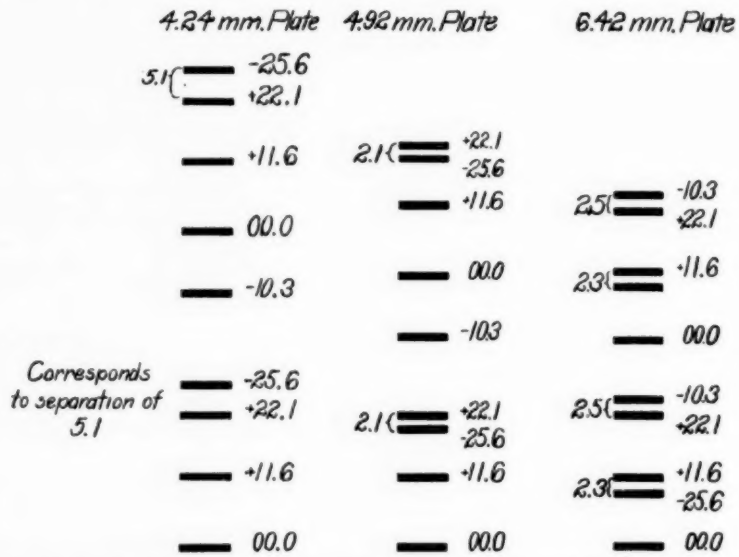


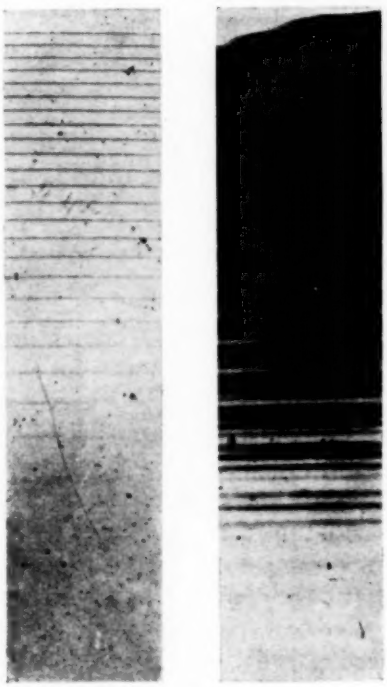
Fig. 3. Pattern for λ2537 in zero magnetic field to be expected from each plate when the ordinary ray (E vertical in our experiment) is used.

In the actual photographs with the 4.24 m/m plate one obtains four fringes three narrow and one wider, the pattern repeating itself over and over. With the 4.92 m/m plate one obtains four fringes, three narrow and the fourth somewhat wider and more dense. The 6.42 m/m plate gives three fringes, one narrow and two wider and more dense. The diagram shows which of the fringes are due to the overlapping of adjacent interference orders.

[8] See Von Baeyer, Phys. Zeits. 9, 831 and F. Simeon, Jour. Sci. Inst. I, 296 for formulas relative to Lummer-Gehrcke plate patterns.

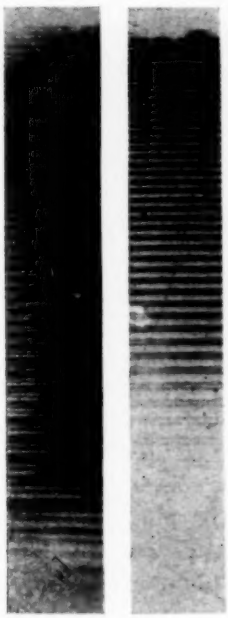
Observations in Zero Magnetic Field

Observations were first made with the exciting light from the arcs polarized with the electric vector vertical and with the stem of the resonance bulb at −18°C. Under these conditions in zero magnetic field the resonance radiation is known to be 80 percent polarized with the major electric vibration vertical. Fig. 4 shows the Lummer-Gehrcke plate patterns obtained using the 4.92 m/m plate. In *A* we have the pattern due to the vertically polarized radiation which shows all four fringes, while in *B* we have the pattern due to the horizontally polarized resonance radiation which shows but one fringe. Later observations have shown that this fringe is the one



B *A*

Fig. 4. Spectrograms obtained with 6.42 mm Lummer-Gehrcke plate.



A *B*

Fig. 5. Spectrograms obtained with 4.92 mm Lummer-Gehrcke plate.

caused by the overlapping of the −25.6 line of one order and the +22.1 line of the next. This definitely proves that the incomplete polarization is due to either or both of the outer hyper-fine structure lines, the three central components being 100 percent polarized in the vertical direction.

The patterns obtained with the 4.24 m/m plate are quite similar to those illustrated and lead to the same conclusions.

Fig. 5 shows the patterns due to the vertically and horizontally polarized radiation when the 6.42 m/m plate is used. In the vertically polarized image all three fringes are visible, as is to be expected. In the horizontally polarized image there are but two fringes, these being the ones caused by the over-

lapping of -10.3 and $+22.1$; and of $+11.6$ and -25.6. However, observations with the thinner plates proved that -10.3 and $+11.6$ do not appear in this pattern consequently we conclude that both the outside lines are responsible for the incomplete polarization of the λ2537A resonance line of mercury.

Similar hyperfine structure patterns were obtained while the stem of the resonance bulb was maintained at 0°C. Under these circumstances the resonance radiation is known to be about 70 percent polarized in the vertical direction. These photographs show that the added intensity in the horizontally polarized beam is distributed over all the five hyperfine structure lines just as we would expect since the further depolarization is due to secondary resonance radiation and perhaps also to collisions. These plates afforded a simple means of identifying the one or two fringes observed in the pattern due to the horizontally polarized light.

Further observations made with the exciting light polarized horizontally show that at low vapor pressures the radiation emitted in the direction of the electric vector of the exciting light is due entirely to the two outside hyperfine structure lines.

Observations in a Magnetic Field Parallel to the Electric Vector of the Exciting Light

For these observations the exciting light was polarized with its electric vector vertical and parallel to the magnetic field. Using the arcs for sources the polarization of the resonance radiation did not sensibly increase with increase of the magnetic field up to 3450 gausses, the maximum field available. The fringe patterns obtained in all the fields up to the maximum appear quite similar to those obtained in zero field. They show that all five components appear in the pattern due to the resonance radiation polarized parallel to the field.

The radiation polarized perpendicular to the field contains, of course, those perpendicular components of the Zeeman patterns which can be excited by the absorption of light polarized parallel to the magnetic field. This perpendicularly polarized radiation contains only the two outside hyperfine structure lines, and it is a surprising fact that each of these shows no sign of splitting in any magnitude of field available.

The simplest explanation of this is afforded by assuming that these outer hyperfine structure lines do not split in a magnetic field and are consequently emitted unpolarized whether excited by light polarized parallel or perpendicular to the magnetic field. However, the truth of this simple explanation appears doubtful in view of the observations of MacNair[5] and the experiment described in the first part of this paper.

In order to clear up this difficulty it appears necessary to study the Zeeman effect of the hyperfine structure lines in absorption.

University of Iowa,
Physics Laboratory,
August 30, 1927.

RECOMBINATION SPECTRA OF ATOMIC IONS AND ELECTRONS*

By F. L. Mohler

Abstract

Method of enhancing recombination in a discharge tube.—Spectra were excited in a thermionic discharge tube containing a fine wire cathode completely inclosed by a cylindrical anode. When operated with low voltage and relatively high current and vapor pressure, high ion concentration and recombination of ions and electrons were favored.

Photographs of recombination spectra of caesium and potassium.—Currents from 0.05 to 0.7 amp. in caesium vapor at pressures from 0.1 to 1 mm gave continuous bands extending to the violet from the limit $2P_1$ of the subordinate series, from the limit of the F series and faintly beyond the P series. The intensity of these bands is rapidly increased by increasing the vapor pressure or the current. Under these conditions the higher series lines are enhanced and the F and D series relatively intense. Lines near the limit become very diffuse and the forbidden series $1S-mD$ is excited. Potassium under similar conditions shows a strong band beyond the subordinate series.

Spectrophotometer measurements in recombination spectra.—Intensities of the continuous spectrum were measured throughout the visible range. The intensity reaches a maximum slightly on the red side of the limits $2P_1$ and $3D_{2,3}$ and decreases regularly and rapidly on the violet side. The two peaks are of the same magnitude with the P peak relatively greater at lower pressures. The intensity is proportional to the square of the current.

The phenomena are qualitatively in accord with theory. The intensity distribution in the line spectrum indicates that there is a relatively high probability of recombination into levels of high quantum number giving radiation in the far infrared. Recombination into the normal level is relatively improbable.

Introduction

PRIOR to 1914 it was commonly assumed that the radiation of electric discharges resulted from recombination of ions and electrons. Bohr's theory and the experiments on excitation by electron collision initiated by Franck and Hertz clearly showed that an important part of the line spectrum radiation of atoms came from excitation without ionization. The theory indicated that recombination would give rise to a continuous spectrum in addition to the line spectrum. If electrons with random values of kinetic energy $mv^2/2$ fall into levels of energy $h\nu_i$ relative to the ionized state as zero, the frequencies emitted are given by the equation

$$h\nu = mv^2/2 + h\nu_i$$

This represents continuous bands extending from each series limit of frequency ν_i to higher frequencies while transitions from the levels ν_i to the normal level will give line emission.

* Publication approved by the Director of the Bureau of Standards of the U. S. Department of Commerce.

As these band spectra are not commonly observed it is probable that recombination usually takes place on the electrodes and tube walls and that the energy is dissipated as heat. There are, however, many references in the literature to spectra ascribed to recombination. Stark[1] describes a continuous spectrum of hydrogen canal rays extending from the limit of the Balmer series which conforms to the theoretical predictions for recombination of atom ions. Balasse[2] describes briefly continuous spectra emitted by caesium and potassium in an induction discharge which he ascribes to recombination. Miss Hayner[3] has explained the unusual intensity distribution in the line spectrum of the mercury arc afterglow on the basis of recombination. The higher members of the subordinate series of triplets actually increase in intensity after the discharge is cut off. Now it is certain that the probability of recombination will increase rapidly as the electron speed is dissipated. Consequently recombination may increase for a while in spite of the continual decrease in electron concentration.

Method and Procedure

The purpose of this research has been to obtain recombination spectra by simply increasing the current in a discharge tube so designed that a relatively high concentration of positive ions could be obtained. Excitation by electron collision will give an intensity of radiation that is proportional to the discharge current while the intensity of the recombination will depend

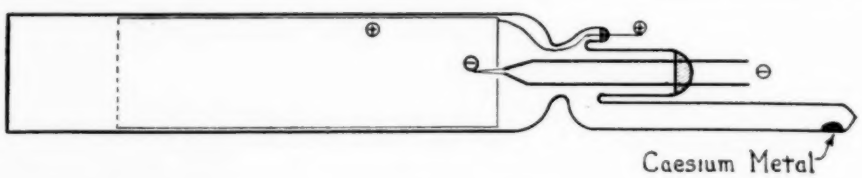


Fig. 1. Thermionic tube used to observe recombination spectra.

on the product of the ion concentration and the electron concentration and will be proportional, to a first approximation, to the square of the current. Consequently a series of exposures with increasing current and proportionately decreasing exposure time should show radiation resulting from collision excitation in equal densities while the effect of recombination will be enhanced with increasing current.

The design of tube adopted for securing high ion concentration makes use of a principle described first by Kingdon[4] and applied by him and by Foote and the author[5] for the sensitive detection of positive ions by their space charge effect. A fine wire cathode is almost completely inclosed by the anode so that positive ions can only be removed from the space by

[1] Stark, Ann. d. Physik **52,** 255 (1917).
[2] Balasse, Comptes rendus, **184,** 1002 (1927).
[3] Hayner, Zeits. f. Physik **35,** 365 (1926).
[4] Kingdon, Phys. Rev. **21,** 408 (1923).
[5] Foote and Mohler, Phys. Rev. **26,** 195 (1925); Mohler and Foote, Phys. Rev. **27,** 37 (1926).

reaching the cathode, and this is so small that ions will make many orbits around the cathode before striking it. In the present research this design of tube (Fig. 1) was used under extreme conditions where Kingdon's simple theory is scarcely applicable.

The tube was of quartz and Pyrex with a platinum anode and 4 mil tungsten cathode. Caesium vapor was selected for the first experiments because of several advantages, the chief one being that a caesiated filament can be operated at a temperature so low that thermal radiation will not mask faint continuous emission by the vapor. Caesium was distilled into the tube in a high vacuum, the tube sealed off and placed in an electric furnace which heated the entire tube to the temperature determining the vapor pressure. Discoloring of the quartz set an upper limit of about 270°C (pressure about 1 mm). The maximum current which could be obtained from the caesiated wire increased rapidly with the vapor pressure from about .1 amp at 200°C to nearly an ampere at the highest vapor pressure. The ionization potential of caesium is 3.9 volts and it was found that 5 volts or less was sufficient to maintain a saturated current which was controlled by the filament temperature.

Photographs of the Recombination Spectrum

With temperatures higher than 195°C (pressure 0.08 mm) and with currents greater than 0.07 amp., or somewhat less at higher pressure, there appears a conspicuous continuous spectrum of the type predicted for recombination. Fig. 2, Nos. 1 to 5 are caesium spectra obtained with a Hilger E_2 quartz spectrograph and panchromatic plates. Three separate bands can be distinguished: one extending from near the limit $2P_1$ of the subordinate series at 5082A toward the violet; a second band, somewhat masked by lines, starts near the limit of the fundamental series, $3D_{2,3}$ at 5948A, while the strongest exposures show a faint band beyond the limit of the principle series $1S$ at 3183A. It was estimated that the intensity near the P limit was of the order of 100 times the intensity beyond the S limit.

Spectra 1 to 4 of Fig. 2 illustrate the enhancement of continuous bands with increasing current, for the exposure times were inversely proportional to the current. The continuous emission also increases in intensity as the vapor pressure is increased. The intensity at 230°C (0.24 mm) was between three and four times that at 200°C (0.09 mm).

The appearance of the discharge changes greatly as the current increases. With low currents the discharge is reddish in color and fills the tube uniformly except for the cathode glow which is very bright in a thin sheath. In photographing the spectra the cathode was focused on the slit. The bright spots on the lines in exposure 1 are the images of this glow. As the current is increased a diffuse yellow white light surrounds the cathode. This is brilliant within about 5 mm of the wire and fades rapidly at greater distances. The spectrograms show the image of the cathode glow as a dark streak in the continuous bands. With a current of 0.7 amp. at 267°C (0.7 mm) the intensity of the yellow glow matched that of an incandescent tungsten strip at about 1500°C.

Fig. 2, No. 6, is a photograph of the potassium spectrum in a similar discharge tube at 280°C (pressure a few tenths mm) and a current of 0.7 amp. The strong continuous band extends from the limit of the subordinate series $2P_{1,2}$ at 4552A. The faint continuous spectrum in the red may come from thermal radiation of the filament. The fundamental series limit falls

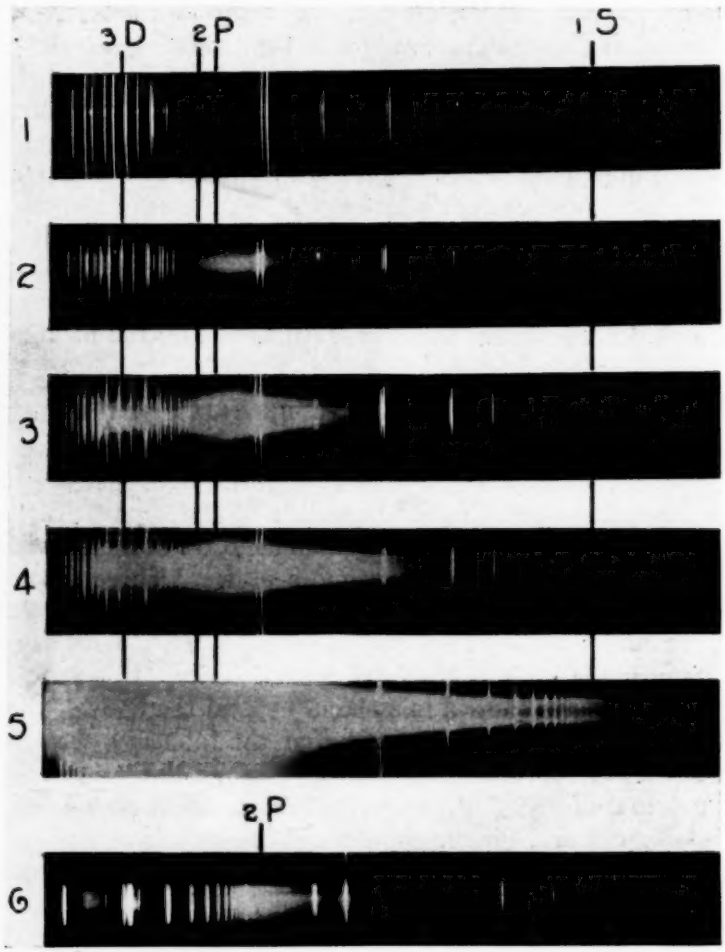


Fig. 2. 1 Cs, 0.015 amp. 160°C (0.03 mm) exposure 4 hours
2 Cs, 0.05 " 230°C (0.24 mm) " 1 hour
3 Cs, 0.2 " 230°C (0.24 mm) " 15 min.
4 Cs, 0.4 " 240°C (0.32 mm) " 8 min.
5 Cs, 0.5 " 240°C (0.32 mm) " 1 hour
6 K, 0.7 " 280°C (0.2 mm?) " 2 hours

outside the range of the panchromatic plate. A few experiments with mercury were inconclusive though there was evidence of a continuous band beyond the subordinate series limit 2^3P_2 at 2491A.

There is a conspicuous change in the line spectra as the current is increased. Fig. 2 shows that higher series lines of caesium become more intense

while the F series and to a lesser extent the D series are enhanced relative to the S and P series. Under magnification it is seen that the lines in each series become more diffuse as they approach the limit until they are completely fused together so that the continuous spectrum begins on the red side of the limit. The point where they become unresolved depends on the current. Thus with 0.09 amp., $2P_1-17D$ at 5043A is visible while at 0.5 amp. $2P_1-15D$ at 5073A is the last line (the limit is at 4943A).

One photograph was made in the first order of a 10 foot grating which showed the broadening in much more detail. In each series the diffuseness increased rapidly near the limit and for corresponding lines of different series it was greatest for the F series and progressively less for the D and S lines. This plate, though underexposed over its entire length, showed many higher series lines not listed in the tables of Paschen and Fowler.

The original negatives obtained with the quartz spectrograph with currents greater than .4 amp show a diffuse line on the violet side of each principal series doublet from $1S$–$3P$ to $1S$–$12P$. This is the "forbidden series" $1S$–mD.

Spectrophotometer Measurements

Measurements of relative intensity in the continuous bands as a function of the wave-length were made by visual spectrophotometry. The intensity of the discharge was matched with a calibrated tungsten strip lamp by varying the current through the lamp. Two arrangements of apparatus were tried. In the first a Lummer-Brodhun spectrophotometer was used to compare the two sources. In the second the light from the discharge was focused in the plane of the tungsten strip and a second achromatic lens accurately focused the strip and image of the discharge on the slit of a large direct vision spectroscope. The field in the spectroscope was thus sharply divided by the strip and this could be matched with any selected point of the discharge. This is the common optical pyrometer principle and it has the advantages of giving the highest possible spectrum resolution, of matching a single point of the source and strip lamp, and of being equally applicable to photographic and visual observations. Computations of intensity, when both temperature and wave-length are variables, are somewhat complicated. The tables and graphs prepared by Frehafer and Snow[6] were used.

Fig. 3 gives some typical results showing both the observed tungsten color temperature required for an intensity match and the computed relative intensities for two conditions of the discharge. There are several factors which cause uncertainty in the measurements. The intensity was low; on the red side of 5000A the settings had to be made between close diffuse emission lines, and in the course of the experiments the quartz window became yellow under the action of the caesium so that probably its absorption in the blue and violet increased greatly. Nevertheless these curves give more definite information than the spectrograms because of the variation of plate sensitivity with wave-length. Thus the maximum density in the continuous spectrum is on the violet side of the subordinate series limits. Actually the

[6] Frehafer and Snow, Bureau of Standards Misc. Pub. 56.

intensity reaches a maximum on the red side of the D series limits as well as the F series limits though the critical spectrum range near both peaks is masked by emission lines. The rapidly increasing diffuseness of lines near the limit entirely masks the abrupt discontinuity which is predicted by theory. It is seen from the curves of color temperature against wave-length that the intensity distribution beyond both series limits is similar to that of a black body of equal intensity being in one instance exactly the same as

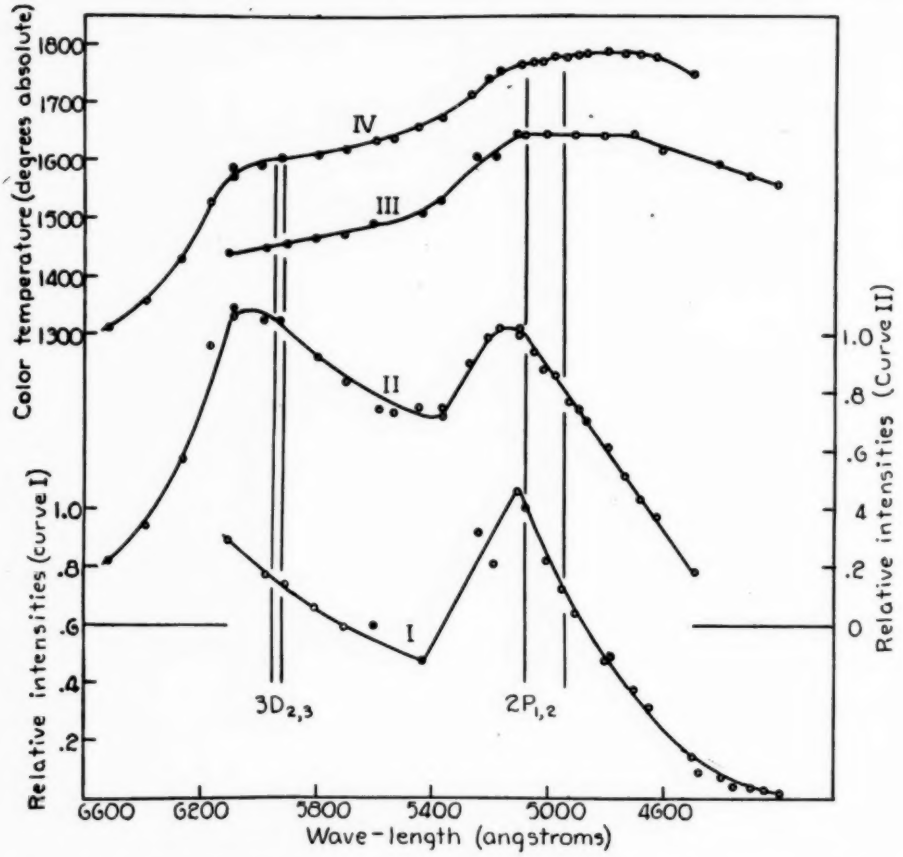


Fig. 3. Photometric measurements of the continuous spectrum of caesium. Curve I relative intensity (left scale) for current 0.4 amp., temperature 245°C (0.37 mm). Curve II, relative intensity (right scale) for current 0.7 amp., temperature 267°C (0.7 mm). Curves III and IV, observed absolute tungsten color temperature of strip lamp for computations of curves I and II, respectively.

the strip lamp over a range of 500 angstroms. There is no certain evidence of a double peak at $2P_{1,2}$ though the points on curve II give a questionable indication of this. There is a noticeable change in the relative intensities of the P and D peaks as the discharge conditions are varied.

A few measurements of the intensity variation with current of the continuous band near 5000A, tube temperature 245°C (0.37 mm) gave the following results: current 0.40, intensity 1.00; current 0.30, intensity 0.54;

current 0.10, intensity 0.063. The ratios of the square of the current to the intensity are 0.160, 0.166 and 0.159, showing that in this limited range the intensity varies as the square of the current.

Discussion of Results

The spectra of these discharges show two classes of phenomena produced by high ion concentration, continuous spectra and line spectra resulting from recombination, and perturbation effects of ions on the atomic energy levels producing diffuseness of lines and a breakdown of selection principles. The latter effects need not be considered further.

The probability that an electron of speed v will recombine with a positive ion can be expressed in terms of an effective collision area $q(v)$ for a collision resulting in recombination, and there will be such a function $q(v\nu_i)$ associated with each atomic level of energy $h\nu_i$ (series limit ν_i). This recombination will be accompanied by emission of radiation of a frequency ν given by the relation

$$h\nu = h\nu_i + mv^2/2 \tag{1}$$

There is a general relation between $q(v\nu_i)$ and the probability $B(\nu\nu_i)$ that an atom in the state corresponding to ν_i will absorb a quantum $h\nu$ giving a free electron of speed v:

$$q(v\nu_i) = \text{const} \times B(\nu\nu_i)\nu^3/(\nu - \nu_i) \tag{2}$$

where v and ν are given by Eq. (1).[7] $B(\nu\nu_i)$ can be measured only for normal energy levels and except in the x-ray range the data are very meager. Measurements of photoionization give $B(\nu)$ as a function of ν for the $1S$ level of caesium[5,8] and show that B decreases rapidly from ν_i to higher values of ν. B is finite at ν_i so that q must approach infinity as v approaches zero. The photoionization data[5] and Eq. (2) show that q for a velocity corresponding to 0.1 volt is twenty times as great as q for 0.5 volt.

The rate of recombination will depend on the product of the ion concentration N^+, the concentration of electrons $N^-(v)$ of velocity v and $v \times q(v\nu_i)$. Each recombination will give a quantum of radiation $h\nu$ so that the intensity is given by

$$I(\nu)d\nu = \text{const} \sum_{\nu_i} N^-(v) \cdot N^+ \cdot vq(v\nu_i) \cdot \nu^{-1} d\nu \tag{3}$$

Since the velocity distribution of electrons $N^-(v)$ is unknown it is not possible to derive from the present data the fundamental atomic functions $q(v\nu_i)$ or $B(\nu\nu_i)$. Some qualitative conclusions can, however, be drawn on the basis of reasonable assumptions as to the electrical conditions in the discharge. Studies of discharge characteristics by Langmuir and Jones[9] and by Comp-

[7] Milne, Phil. Mag. **47**, 209 (1924).
[8] Little, Phys. Rev. **30**, 109 (1927).
[9] Langmuir and Jones, Sci. **59**, 380 (1924).

ton and Eckart[10] suggest the following conclusions though conditions are scarcely comparable.

The potential drop (about 5 volts) is chiefly in the thin cathode sheath and the rest of the space is probably at a nearly uniform potential. Current voltage curves indicate that the maximum space potential is not much different from that of the anode and both ions and electrons must be removed from the space largely at the anode. Thus their concentration will be high near the axis of the tube and low near the anode with nearly equal concentrations of both at each point since the potential gradient is low. Electron velocities are probably low since few electrons will have speeds greater than the first resonance potential 1.4 volts and the low gradient favors accumulation of very slow electrons. Increasing the pressure will decrease the average electron speed and the rate of diffusion and increase the concentration of ions and electrons.

The form of the yellow recombination glow, bright at the center except in the cathode sheath and fading rapidly away from the center, is consistent with the prediction as to distribution of ions. The observed increase in intensity proportional to the square of the current is in accord with Eq. (3) if we assume that electron and ion concentrations are proportional to the current. This simple relation, however, cannot hold over a wide range. The enhancement of recombination with pressure results from the increased concentration and the decreased electron speed. The observed change in relative heights of P and D peaks in Fig. 3 under different conditions can only result from a change in the average electron speed. The speed is probably lower in curve II taken at higher pressure which means that $vq(v)$ is relatively greater for the D levels at low speed.

The intensity of the higher series lines and of the F series shows that many electrons fall into orbits of high total and azimuth quantum numbers, and the continuous spectrum must extend into the far infrared. The results suggest that the maximum intensity is in the P and D peaks and shifts toward the red with decreasing electron speed. However the total effect of all bands originating in the infrared is very nearly zero at 6600A. Recombination into the normal $1S$ level is relatively improbable but since caesium vapor absorbs this radiation the observed intensity may be misleading. At least it is certain the computations of recombination based on observed values of B for normal vapor will not give even the right magnitude for the total recombination.

The research reported in this paper is being continued with the hope that it will be possible on the basis of electrical measurements of discharge conditions to make quantitative estimates of the various factors entering into Eq. (3). The author is indebted to Dr. Meggers and to Dr. Wensel of this Bureau for assistance in the spectroscopic and photometric work.

BUREAU OF STANDARDS,
December 3, 1927.

[10] Compton and Eckart, Phys. Rev. **25**, 136 (1925).

A NOTE ON THE ZEEMAN EFFECT IN BAND SPECTRA

By R. de L. Kronig

Abstract

An explanation is given for the peculiar behavior of the intensities of the Zeeman components in the Ångström CO bands recently investigated by Kemble, Mullikan and Crawford. The phenomenon referred to is found to furnish a further confirmation of the assumptions on which the theory of the Zeeman effect in band spectra is based.

IN A recent paper Kemble, Mulliken, and Crawford[1] have discussed the general theory of the Zeeman effect in the band spectra of diatomic molecules. They consider the molecule as possessing a moment of momentum $nh/2\pi$ around the line joining the nuclei so that in its temperature rotation it will behave like a symmetrical top, the total moment of momentum being $jh/2\pi$ $(j \geqq n)$. In the presence of a magnetic field H it will then suffer a space quantization, its moment of momentum along the direction of the field becoming $mh/2\pi$ $(|m| \leqq j)$. These authors have also investigated experimentally the Zeeman effect in three bands ${}^1S \rightarrow {}^1P$ of CO, since for transitions of this type the assumptions on which the theory is based will be very nearly fulfilled. Here $n=0$ for the initial state, $n=-1$ for the final state[2] so that the magnetic moment of the molecule along the line joining the nuclei is zero for the former and one Bohr magneton μ_1 for the latter (μ_1 being considered as positive). The energy of rotation in the two states is given by

$$W_j^0 = \frac{h^2}{8\pi^2 I} j(j+1), \quad W_j^0 = \frac{h^2}{8\pi^2 I_1}[j(j+1)-1], \tag{1}$$

where j takes the values 0, 1, 2, $\cdots$ in the first case, 1, 2, $\cdots$ in the second, and I and I_1 denote the respective moments of inertia. In the magnetic field the initial state suffers no resolution, while the final state is split into $2j+1$ components with the magnetic energies

$$W_{jm}{}^1 = m\mu_1/j(j+1). \tag{2}$$

If the z-axis be chosen parallel to the magnetic field, the amplitudes for the various transitions starting from a state jm of the upper level ${}^1S$ (called l) to the various states $j'm'$ of the lower level ${}^1P$ (called l_1) are given by[3]

[1] E. C. Kemble, R. S. Mulliken, and F. H. Crawford, Phys. Rev. **30**, 438 (1927).

[2] We might also have chosen $n=+1$. Since, however, the magnetic moment also reverses sign if the sign of n is changed, the results arrived at are found to be the same as with $n=-1$.

[3] A knowledge of the intensities alone is not sufficient for the subsequent perturbation calculations; the amplitudes themselves have to be used. They have been given in a previous paper of the author, (Zeits. f. Physik **45**, 458 (1927).

$$\left.\begin{aligned} P_x^0(l\,j\,m,\ l_1\,j+1\,m\mp1) &= \mp\frac{a}{4}\left(\frac{(j+2)(j\mp m+2)(j\mp m+1)}{(j+1)(2j+1)(2j+3)}\right)^{1/2}, \\ P_z^0(l\,j\,m,\ l_1\,j+1\,m) &= -\frac{a}{2}\left(\frac{(j+2)[(j+1)^2-m^2]}{(j+1)(2j+1)(2j+3)}\right)^{1/2} \end{aligned}\right\} \tag{3}$$

$$\left.\begin{aligned} P_x^0(l\,j\,m,\ l_1\,j\,m\mp1) &= -\frac{a}{4}\left(\frac{(j\mp m+1)(j\pm m)}{j(j+1)}\right)^{1/2} \\ P_z^0(l\,j\,m,\ l_1\,j\,m) &= -\frac{a}{2}\frac{m}{[j(j+1)]^{1/2}}, \end{aligned}\right\} \tag{4}$$

$$\left.\begin{aligned} P_x^0(l\,j\,m,\ l_1\,j-1\,m\mp1) &= \mp\frac{a}{4}\left(\frac{(j-1)(j\pm m)(j\pm m-1)}{j(2j-1)(2j+1)}\right)^{1/2}, \\ P_z^0(l\,j\,m,\ l_1\,j-1\,m) &= \frac{a}{2}\left(\frac{(j-1)(j^2-m^2)}{j(2j-1)(2j+1)}\right)^{1/2}, \end{aligned}\right\} \tag{5}$$

Eq. (3) referring to the P-branch, Eq. (4) to the Q-branch, Eq. (5) to the R-branch.

Kemble, Mulliken, and Crawford are able to interpret their Zeeman patterns on the basis of Eq. (2). For the intensities, however, they find some curious anomalies which are not in harmony with Eqs. (3), (4), (5). Thus their measurements show beyond doubt that in parallel polarization the low-frequency components in a resolved line of the Q-branch have a distinctly greater intensity than the symmetrically situated high-frequency components, the difference becoming less marked as j increases, while according to Eqs. (3), (4), (5) the intensities in the Zeeman pattern of each line should be quite symmetrical. To explain this behavior, one must remember that the expressions (3), (4), (5) are accurately valid only in the limiting case $H=0$, because the magnetic field itself alters the intensities of the components. If the change produced in the amplitude P be P^1H, then since the intensity is proportional to P^2, the relative change in the intensity will in first approximation be

$$\epsilon=[(P^0+P^1H)^2-(P^0)^2]/(P^0)^2\sim 2P^1H/P^0. \tag{6}$$

P^1, however, can be obtained from perturbation calculations,[4] according to which for any pair of states ss'

$$P^1(ss')=\frac{1}{h}\sum_{s''}{}'\left[\frac{H^1(ss'')P^0(s''s')}{\nu_0(ss'')}-\frac{P^0(ss'')H^1(s''s')}{\nu_0(s''s')}\right], \tag{7}$$

where H^1 denotes the perturbation energy, while the accent at the summation sign signifies that terms with zero denominator are to be omitted. In our case

[4] M. Born, W. Heisenberg, P. Jordan, Zeits. f. Physik **35**, 557 (1926).

$$H^1(ss') = -M^0(ss'), \tag{8}$$

M being the magnetic moment of the molecule.

In (6) the terms with pure rotation frequencies in the denominator will by far exceed all others so that we need to consider them alone. For a transition $ljm \rightarrow l_1jm$, *i.e.*, for a parallel component of the Q-branch, we find for example

$$P_z^1(ljm,\ l_1jm) = \frac{1}{h}\left[\frac{P_z^0(ljm,\ l_1j+1m)M_z^0(l_1j+1m,\ l_1jm)}{\nu_0(l_1j+1,\ l_1j)} + \frac{P_z^0(ljm,\ l_1j-1m)M_z^0(l_1j-1m,\ l_1jm)}{\nu_0(l_1j-1,\ l_1j)}\right].$$

The components of the magnetic moment are given by expressions quite analogous to (3), (4), (5), the only one interesting us here being

$$M_z^0(l_1jm,\ l_1j-1m) = \mu_1\left(\frac{(j^2-1)(j^2-m^2)}{j^2(2j-1)(2j+1)}\right)^{1/2}. \tag{9}$$

From Eqs. (6) and (7) we find thus with the aid of Eqs. (1), (3), (4), (5), (8), (9)

$$\epsilon_x(ljm,\ l_1j+1\ m\mp1) = \mp\frac{8\pi^2\mu_1 I_1 H}{h^2}\,\frac{j\pm m}{(j+1)^2},$$

$$\epsilon_z(ljm,\ l_1j+1\ m) = -\frac{8\pi^2\mu_1 I_1 H}{h^2}\,\frac{m}{(j+1)^2},$$

$$\epsilon_x(ljm,\ l_1jm\mp1) = \mp\frac{8\pi^2\mu_1 I_1 H}{h^2}\left[\frac{(j^2-1)(j\pm m-1)}{j^2(2j-1)(2j+1)} - \frac{j(j+2)(j\mp m+2)}{(j+1)^2(2j+1)(2j+3)}\right],$$

$$\epsilon_z(ljm,\ l_1jm) = \frac{8\pi^2\mu_1 I_1 H}{h^2}\left[\frac{(j^2-1)(j^2-m^2)}{j^2(2j-1)(2j+1)m} + \frac{j(j+2)[(j+1)^2-m^2]}{(j+1)^2(2j+1)(2j+3)m}\right],$$

$$\epsilon_x(ljm,\ l_1j-1\,m\mp1) = \pm\frac{8\pi^2\mu_1 I_1 H}{h^2}\,\frac{j\mp m+1}{j^2},$$

$$\epsilon_z(ljm,\ l_1j-1\,m) = -\frac{8\pi^2\mu_1 I_1 H}{h^2}\,\frac{m}{j^2}.$$

These expressions signify an unsymmetrical change in the intensities of the Zeeman patterns of such a kind that the components on one side of the original line gain in strength what the symmetrically situated ones lose. The relative change has the order of magnitude

$$\frac{\mu_1 H}{h} \Big/ \frac{hj}{4\pi^2 I_1},$$

i.e., the ratio of the precession frequency in the magnetic field to the frequency of rotation of the molecule, just as one would have it in the classical theory. Thus with increasing j the relative change decreases as observed. The ratio itself for $j=1$, for a field of 30000 gauss, and a moment of inertia 10^{-39}, is of the order of magnitude 1/4 so that the intensity changes should be quite noticeable. $\epsilon_z\,(ljm, l_1jm)$ is positive for positive values of m, negative for negative values of m, *i.e.*, the parallel components of the Q-branch corresponding to positive values of m should be stronger than those corresponding to negative values. The former are, however, the low-frequency components, since positive values of m signify according to Eq. (2) larger energy values of the final state. The perpendicular components behave in just the opposite way. The results obtained by Kemble, Mulliken and Crawford are thus fully understood. Similar considerations apply to the components of the other branches, where, however, no clear indications are available as to how the intensities change.

The considerations given here show that the assumptions by means of which one has tried to interpret the Zeeman effect in band spectra lead to an understanding even of the finer details in the observed patterns. Moreover they illustrate how the intensity formulas lose their accurate validity if two precessions of comparable frequencies are superimposed.

I am indebted to the National Research Council and the International Education Board for the grant of a travelling fellowship.

UNIVERSITETETS INSTITUT FOR TEORETISK FYSIK,
COPENHAGEN,
November, 1927.

CRITICAL PRIMARY VELOCITIES IN THE SECONDARY ELECTRON EMISSION OF TUNGSTEN

By Hermann E. Krefft

Abstract

The secondary electron emission of tungsten has been studied at temperatures up to 1480°K under a vacuum of 10^{-8} mm of Hg, using a tube specially designed to give a surface as free as possible from gas layers. The curve showing the number, n, of secondary electrons produced by one primary electron as a function of the primary velocity, taken with tungsten at 1250° to 1450°K and in the velocity range of 10 to 700 volts has a maximum at 15.3 volts, a minimum at 20 volts and 18 breaks between 25 and 600 volts which have not been observed hitherto. There is a good agreement between these breaks and the inflections found by Richardson and Chalklin in the soft x-radiation of tungsten. A comparison with computed values for the N and O-energy levels of tungsten gives good evidence that some of the breaks are due to these levels. The maximum of the secondary emission curve is found near 630 volts primary velocity. With cold tungsten, as long as the surface has taken on but little gas, a few additional breaks are obtained besides those found with hot tungsten. Generally, with cold, well degassed tungsten the breaks are more intensive. None of these breaks appear when a large amount of gas is on the surface. With hot tungsten n is reproducible to within 0.1 percent, if operating conditions are not changed and if the tungsten is heated sufficiently long before measuring. With two different targets n is found to be different, having maximum values of 1.29 and 1.40. The *effect of adsorption of gas* is to increase n for low velocities, while for higher velocities the reverse is true. Both with cold and hot target n varies with time, as long as adsorption or liberation of gas takes place. The variation of n with time may be thus used to follow up adsorption or liberation of gas by a metallic surface in a high vacuum. The shape of the secondary emission curve in the range of 10 to 25 volts primary velocity is due to adsorbed gases. There is a maximum at 15.5 volts with cold, well degassed tungsten, which is also observed even at the highest temperatures produced. This maximum is perhaps due to a surface layer of oxygen molecules. Judging by the secondary emission the surface of tungsten cannot be considered as entirely freed from gas at temperatures up to 1500°K.

1. Introduction

THE photoelectric measurement of the soft x-radiation of metals excited by slow cathode rays has been used by several observers for the determination of atomic energy levels not accessible to spectroscopic methods. At velocities characteristic of the metal the curve giving the number of photoelectrons produced by one electron striking the metal as a function of its velocity has sudden changes of slope indicating the emission of characteristic radiation. Some of these changes of slope agree fairly well with computed atomic energy levels of the metal.

Besides soft x-radiation there is emission of electrons due to the bombardment of the metal. This emission will be referred to as secondary emission, as long as there is no necessity of distinguishing between its different components. In case of the secondary electron emission previous work does not

definitely show whether there are discontinuities in the slope of the secondary emission curve; *i.e.* the curve giving the number of secondary electrons per primary as a function of the primary velocity, which correspond to those of the soft x-radiation. In a recent investigation[1,2] of the secondary emission curves of a number of metals some breaks were found. However, these breaks do not at all agree with the ones appearing in the soft x-radiation.

The greater number of recent investigations have been carried out with arrangements where it was possible to heat the metal to redness under vacuum shortly before starting measurements. This treatment of the metal was found to have a large influence on the general features of the secondary emission curve. Evidently, gases on the metal greatly change its properties with respect to secondary emission. However, even after heating in a good vacuum the surface of the cold metal cannot be regarded as entirely clean. No matter how good the vacuum is, there will be sufficient gas in the tube partly or entirely to cover the surface of the metal.

In order to make sure that the surface is well degassed, a good plan is to measure the secondary emission while the metal is at a sufficiently high temperature. In this way the secondary emission curve of tungsten has been taken at primary velocities of from 10 to 700 volts. Under such conditions a number of interesting phenomena are observed which have not been found hitherto, on account of gas layers covering the surface of the metal. When measured with a well degassed surface, the secondary emission curve of tungsten has discontinuities, some of which agree well with those found in the soft x-radiation, and with computed values of its *N* and *O* energy levels.

2. Apparatus

The tube used for the final measurements was made of G-702-P glass; no ground joints or cemented connections were used in its design. The electrons emerging from the hot cathode, *K*, (Fig. 1) are accelerated by the electrode *A*, some of them striking the target *T*, after passing through a hole in the center of *A* and through a canal made of nickel, 25 mm long and with a bore of 2.5 mm, fastened to *B*. The target is surrounded by a cylindrical electrode, *C*, receiving only electrons emitted from the target. The cathode consists of a spiral of 10 mil tungsten wire the axis of which coincides with the direction of the primary beam. There is a voltage drop across the cathode of 2.3 volts, the heating current amounting to about 6 amperes. The target forming the bottom of a tungsten cylinder 12 mm long, supported by tungsten wires, is 12 mm in diameter and made of a thin tungsten sheet. The target is heated only by radiation from a tungsten strip, *H*, inside of the cylinder. The voltage drop across the strip is about 5 volts, the heating current varying between 13 and 16 amperes. The distance between *K* and *T* is about 60 mm.

The heating currents are drawn from storage batteries of large capacity. A high voltage storage battery is used for accelerating the primary electrons.

[1] R. L. Petry, Phys. Rev., **26**, 346 (1925).
[2] R. L. Petry, Phys. Rev., **28**, 362 (1926).

The primary voltage consists of two parts, a fixed one, measured by V_1 and a variable one measured by V_2, both voltmeters being correct to within 0.2 percent. The primary current is measured with the galvanometer at G_1, the secondary current is measured with the same galvanometer transferred to G_2 by throwing a switch, thus eliminating changes of sensitivity. Depending on the potentials V_1 and V_2 the primary current varies from 1 to 5 microamperes. In all cases the target has the same potential as the canal, while C is made a few volts positive with respect to the target. The potential of the electrode, A, is always 100 to 200 volts higher than that of the canal or the target. During a run the potential difference between A and B remains constant. The strip H is 10 volts positive with respect to the target.

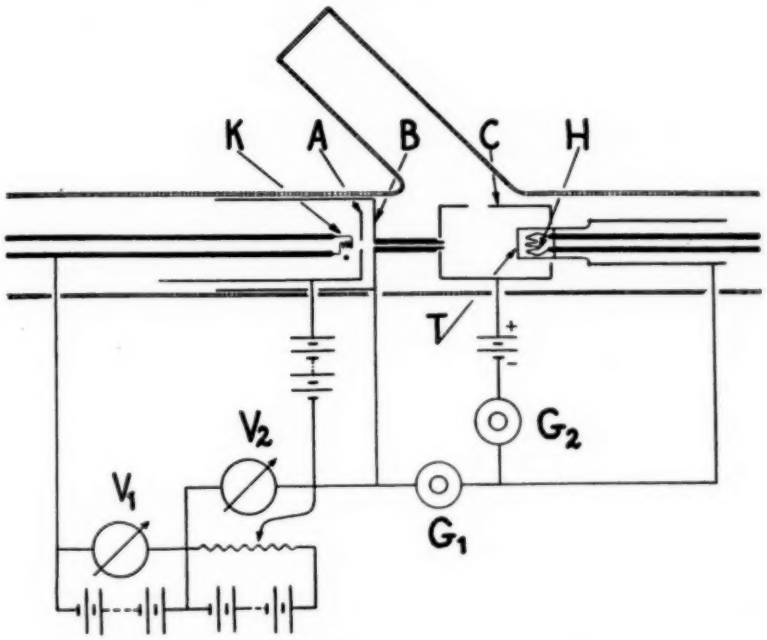


Fig. 1. Diagram of tube and electrical connections.

After the tube is alternately baked at 450°C and operated several times, it is sealed off with a tube containing some charcoal. The vacuum is then maintained only by immersing the charcoal in liquid air. Under such conditions it is not necessary to keep liquid air on the charcoal continuously, since operating the tube for a half-hour with liquid air on the charcoal will restore the vacuum.

An accurate check on the vacuum is obtained by means of a measurement of the ionization current to a thin molybdenum wire placed near the cathode and made negative with respect to the cathode. Through comparison with a sensitive McLeod gauge it was concluded that the vacuum, while measurements are taken, was of the order of 10^{-8} mm Hg. The magnitude of the ionization current depends only slightly on the temperature of the target.

The temperature of the target is determined to within 5° by an optical pyrometer sighted through a polished window fused on a side tube.

3. General Shape of Secondary Emission Curve

The general features of the secondary emission curve of tungsten are shown in Fig. 2. Curves I and II, the experimental points of which are not given on account of the smallness of the scale, were taken with two different targets under the same operating conditions and at a temperature of about 1250°K. There is a considerable change of slope between 60 and 70 volts primary velocity, and both curves have a maximum at about 630 volts, the position of which is not easy to determine exactly, as there is only a slight curvature in this velocity range. The maximum number of secondary elec-

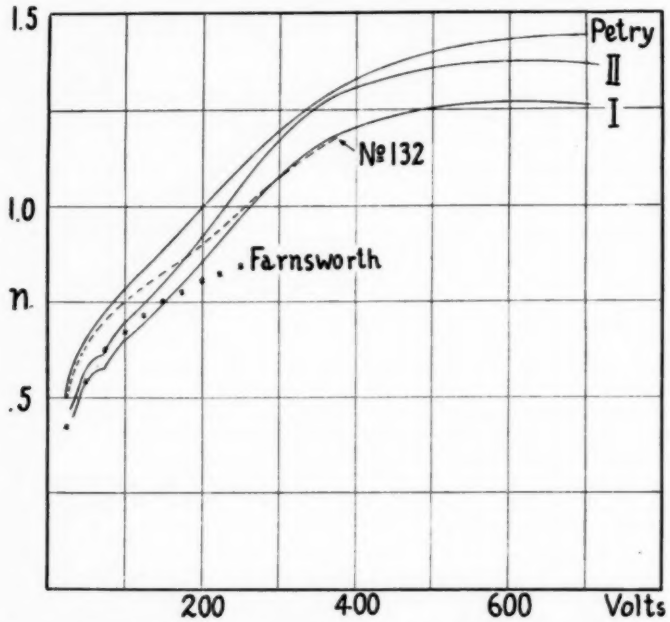


Fig. 2. General trend of secondary emission curve of tungsten, 25 to 700 volts primary velocity. Curve I, target No. I, $T=1250°K$; Curve II, target No. II, $T=1270°K$; No. 132, cold tungsten, target No. II. Measurements of Petry and Farnsworth with cold tungsten.

trons produced by one primary is 1.294 in one case, 1.400 in the other. Curve No. 132 of Fig. 2 is taken with cold tungsten and with the same target as No. II. At low primary velocities the secondary emission of cold tungsten is larger than for hot tungsten; at higher velocities the reverse is true. Above 300 volts curve No. 132 is nearly identical with curve No. I. There was comparatively little gas on the target in case of curve No. 132. If more gas is allowed to get on the target, the maximum of the secondary emission curve may be found at primary velocities down to 200 volts.

The curve determined by Petry[2] with cold tungsten is in fairly good agreement with the curves shown in Fig. 2. Neither Petry nor Farnsworth[3] found

[3] H. E. Farnsworth, Phys. Rev., **25**, 41 (1925).

the strong inflection near 65 volts. This inflection does not appear on curve No. 132, taken with cold tungsten.

The number, n, of secondary electrons per primary depends slightly on the potential applied between the target and C, even if C is positive. If the potential of C is raised from +1 volt to +6 volts, n is increased by about 2 percent. A further variation from +6 volts to +10 volts increases n by another 0.5 percent.

4. Accuracy in Reproduction of n

The number, n, of secondary electrons produced by one primary electron was found to depend quite considerably on the operating conditions of the tube, especially on the retarding field between B and A and on the magnitude of the current to A. The reason is that the primary beam is not entirely

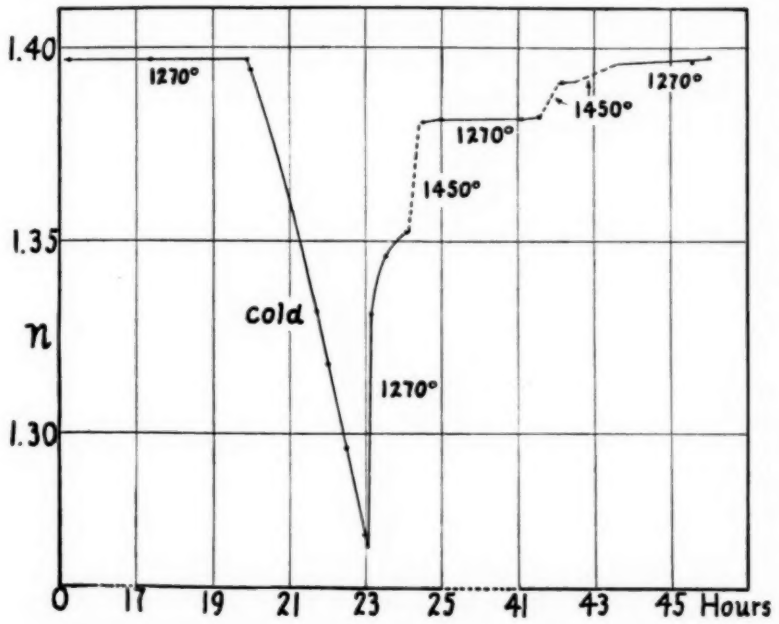


Fig. 3. Effect on n of adsorption and liberation of gases. Variation of n with time. Primary velocity of 600 volts.

homogeneous, because of secondary emission from the edges of A and from the canal. Thus, a certain percentage of the primary electrons have lower velocities than that corresponding to the accelerating potential. If operating conditions of the tube are kept constant, *i.e.* potential between B and A, current to A, temperature of the target, degree of vacuum and potential of C, n is reproducible with unusual accuracy. This is shown very strikingly by the curve of Fig. 3, where the variation of n with time for hot and cold tungsten was measured. Before starting this run, the target was heated for one hour at 1450°K. The discharge of the tube was interrupted only during the night, the charcoal, however, was kept in liquid air all the time. With cold

target, n varies greatly with time, because of adsorption of gases which are liberated by the discharge in the tube. When the tube was not operated the vacuum remained too high to produce a measurable influence on n, even in the course of a night. At the primary velocity of this run n decreases while the amount of gas adsorbed increases. Only at low primary velocities does n increase. With hot target n increases again in the course of time, this behavior of n indicating a gradual liberation of gas. At a higher temperature this process takes place more quickly. After a sufficient length of time the original value of n is restored within one-tenth of a percent.

Even at high temperatures n varies measurably if the target is heated long enough. Evidently, after heating for a considerable length of time at 1450°K, tungsten is not entirely freed from adsorbed gases, which agrees with other experiences regarding an adsorbed layer of oxygen on tungsten. Heating at 1450°K for two hours seems to produce an equilibrium state of the surface. The target, therefore, has to be heated for this length of time, if possible at a higher temperature than during measurements, in order to permit of exactly reproducing n. The design of the tube makes it impossible to heat the target above 1500°K.

TABLE I

Comparison of secondary emission from two targets.

Primary Velocity in volts	Target No. I n_I	Target No. II n_{II}	n_{II}/n_I
50	0.5465	0.5775	1.0565
100	0.6478	0.6992	1.0790
200	0.8620	0.9250	1.0730
300	1.0915	1.1525	1.0555
400	1.2195	1.2925	1.0600
500	1.2750	1.3830	1.0850
600	1.2930	1.4030	1.0850
700	1.2910	1.3980	1.0825

The secondary emission of different targets is not the same as far as n is concerned. In Table I the ratios of the values of n for two different targets are given for various primary velocities. These ratios are nearly constant. The values n_I and n_{II} are picked out at random from a large number of measurements which were carried out at about 1250°K under not entirely identical experimental conditions. This may account for the slight variation of the ratio n_{II}/n_I.

5. MEASUREMENTS

Four sets of runs were taken in the range of 10 to 700 volts primary velocity, one with cold tungsten, the other three at 1270°K, 1340°K and 1410°K. The primary velocity was varied in steps of 0.5 volt between 10 and 25 volts, 1 volt between 25 and 80 volts, 2 volts between 80 and 150 volts, and 5 volts at higher velocities. The secondary emission curve of tungsten thus measured shows a number of discontinuities or breaks which can be

reproduced very accurately. The breaks that appeared with the above variation of the primary voltage were more closely investigated. In all about two hundred runs were made to determine the data shown. In addition to these four sets of runs a large number of observations were made dealing with a more accurate determination of several breaks. Some runs were taken, in order to study the influence of adsorption of gases. In numerous cases the operating conditions of the tube were varied. None of these variations affected either the position or the appearance of the breaks. In

TABLE II

Comparison of breaks in secondary emission with breaks in soft x-radiation and computed energy levels of tungsten.

Critical potentials in secondary emission (volts)	Sign	Critical potentials in soft x-radiation (volts) uncorr.	corr.	ν/R-values of critical potentials in secondary emission	Bohr and Coster	Nishina
30.1	+	31.94	36.84	2.18		
33.4	+	35.4	40.3	2.44	$N_{43,44}=2.5$	
38.7	+	40.0	44.9	2.86	$O_{21,22}=2.9$	$N_{44}=2.8$
						$N_{43}=2.9$
60.3	+			4.46		
64.8	+	65.9	70.8	4.79		
69.3	+			5.12	$O_{11}=5.2$	$O_{21,22}=5.2$
74.8				5.53		$O_{11}=5.7$
92*						
109.2	−	103.3	108.2	8.08		
127.7		122.8	127.7	9.44		
140* 160*		145	150			
190*	+	186	191			
210*						
237.5	+	240.3	245.2	17.56	$N_{23}=17.8$	
249.0				18.40	$N_{22}=18.7$	$N_{23}=18.4$
257.5		258.8	263.7	19.04		$N_{22}=18.8$
275*						
330* 350*		331	336			
390*		390	395			
415		414	419	30.7	$N_{22}=30.6$	
446				33.0		$N_{22}=33.0$
457				33.8		
495	+			36.6	$N_{21}=35.6$	
523	−			38.7		$N_{21}=38.0$
590				43.6	$N_{11}=43.6$	$N_{11}=44.1$

* Disappears at higher temperatures.

the beginning, several runs covering the whole velocity range were taken with a target of 0.05 mm tungsten sheet (target No. I). This being done, the tube was cut open and another target of 0.025 mm thickness (target No. II) was put in its place. The greater part of the measurements referred to in this paper have been carried out with this target No. II.

Part of the final measurements are shown in Figs. 4 to 12. The experimental conditions for these curves are given in the captions, where V is the potential of both B and the target, e_A the potential of A and e_C the collecting potential applied between the target and C. If not otherwise indicated, these

runs were taken with target No. II. In the curves the voltage applied between the negative end of the cathode and the target is given as primary velocity. The number, n, of secondary electrons produced by one primary electron is obtained as the ratio of secondary and primary current.

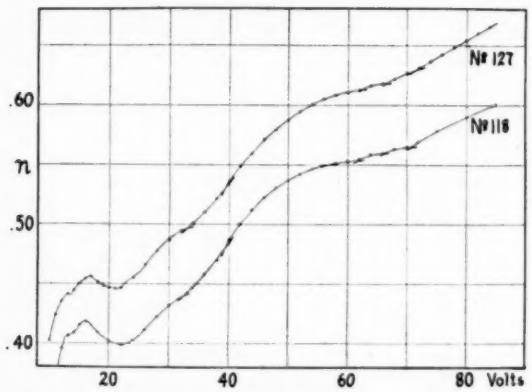


Fig. 4. Secondary emission curve of tungsten for primary velocity range of 10 to 85 volts. No. 118, $T=1250°K$, $e_A=V+200$ volts, $e_C=+2$ volts, target No. I; No. 127, $T=1450°K$ $e_A=V+100$ volts, $e_C=+4$ volts, target No. II.

The potentials of breaks found in the region of 25 to 700 volts primary velocity are given in the first column of Table II. These values have been corrected for voltage drop of the cathode and initial velocity. Since the accelerating potential was applied to the negative end of the cathode this

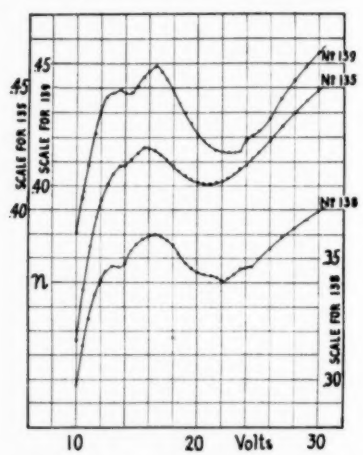


Fig. 5. Secondary emission curve of tungsten, primary velocity range of 10 to 30 volts. No. 135, $T=1270°K$, $e_A=V+100$ volts, $e_C=+1$ volt; No. 138, $T=1270°K$, $e_A=V+100$ volts, $e_C=-4$ volts; No. 139, cold tungsten, $e_A=V+100$ volts. $e_C=+1$ volt.

correction is about -1 volt. Direct measurement of this total correction indicated that there was not an appreciable contact potential between the cathode and the target. The critical primary velocities given in Table II are means taken from four to six single measurements. The signs + and −

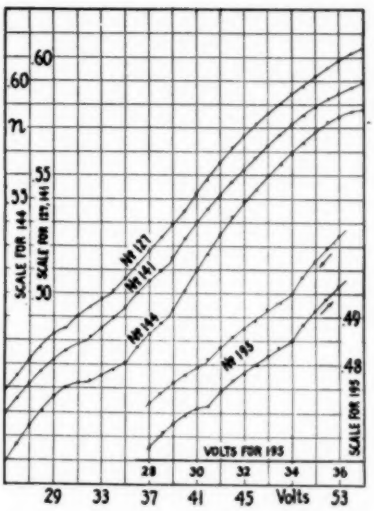


Fig. 6. Secondary emission curve of tungsten, primary velocity range of 25 to 55 volts. No. 127, $T=1450°K$, $e_A=V+100$ volts, $e_C=+4$ volts; No. 141, $T=1340°K$, $e_A=V+200$ volts, $e_C=+4$ volts; No. 144, cold tungsten, $e_A=V+200$ volts, $e_C=+4$ volts; No. 195 $T=1270°K$, $e_A=V+150$ volts, $e_C=+4$ volts.

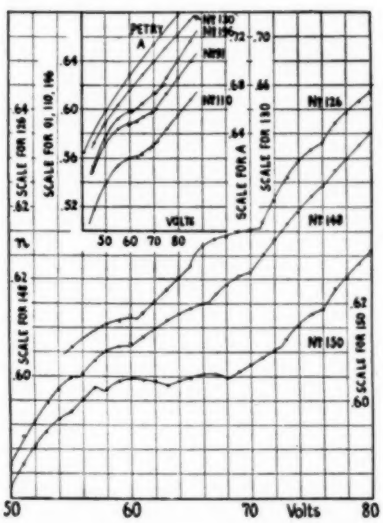


Fig. 7. Secondary emission curve of tungsten, primary velocity range of 50 to 80 volts. No. 91, $T=1450°K$, $e_A=100$ volts, $e_C=+6$ volts, taken with tube with ground joints. No. 110, $T=1250°K$, $e_A=V+200$ volts, $e_C=+6$ volts, target No. I; No. 130, cold tungsten, $e_A=V+200$ volts, $e_C=+10$ volts, large amount of gas on surface, target No. II; No. 196, $T=1270°K$, $e_A=V+150$ volts, $e_C=+6$ volts, target No. II; No. 126, $T=1480°K$, $e_A=V+200$ volts, $e_C=+10$ volts; No. 148, $T=1410°K$, $e_A=V+200$ volts, $e_C=+6$ volts; No. 150, cold tungsten, $e_A=V+200$ volts, $e_C=+6$ volts.

in the second column indicate an increase or a decrease of slope. In some cases it is not possible to decide whether there is a change of slope or not. A number of breaks obtained with cold tungsten disappear at higher temperatures. Except for the regions between 57 and 68 volts and above 475 volts, the secondary emission curve of cold tungsten is similar to that of hot tung-

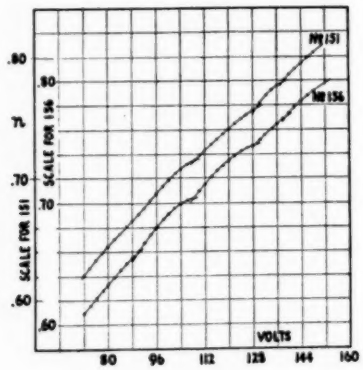


Fig. 8. Secondary emission curve of tungsten, primary velocity range of 75 to 150 volts. No. 151, $T=1270°K$, $e_A=V+200$ volts, $e_C=+10$ volts; No. 156, cold tungsten, $e_A=V+200$ volts, $e_C=+10$ volts.

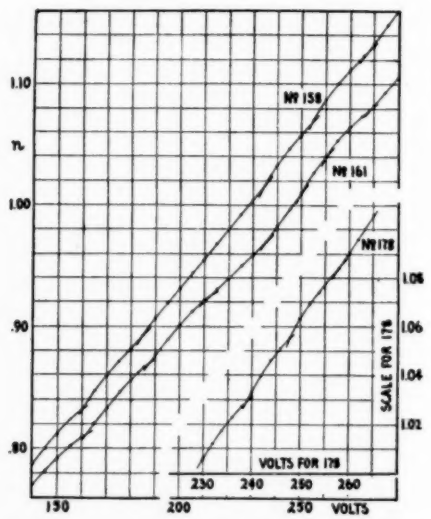


Fig. 9. Secondary emission curve of tungsten, primary velocity range of 140 to 290 volts. No. 158, $T=1410°K$, $e_A=V+200$ volts, $e_C=+10$ volts; No. 161, cold tungsten, $e_A=V+200$ volts, $e_C=+10$ volts; No. 178, $T=1450°K$, $e_A=V+200$ volts, $e_C=+10$ volts.

sten. All the breaks measured with hot tungsten are also obtained with a cold target shortly after heating; some of them are even more marked in the latter case. There can be only a small amount of gas on the tungsten surface, as these measurements were started about a half-hour after heating. In the course of a run the amount of gas on the target increases, and, conse-

quently, n changes its value gradually. As mentioned above, the gases adsorbed by the target are liberated from other electrodes by the discharge in the tube. Therefore, n varies with time more rapidly for higher primary

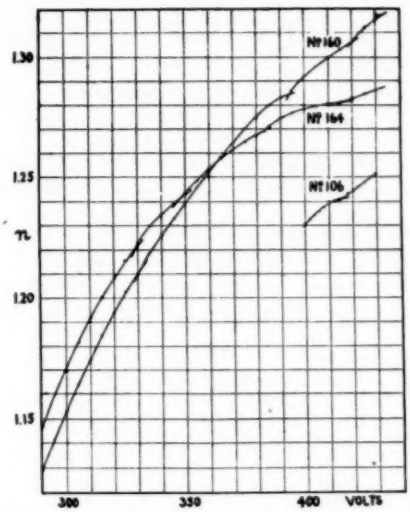


Fig. 10. Secondary emission curve of tungsten, primary velocity range of 280 to 430 volts. No. 106, $T=1450°K$, $e_A=V+200$ volts, $e_C=+10$ volts, target No. I; No. 160, $T=1270°K$, $e_A=V+200$ volts, $e_C=+10$ volts; No. 164, cold, $e_A=V+200$ volts, $e_C=+10$ volts.

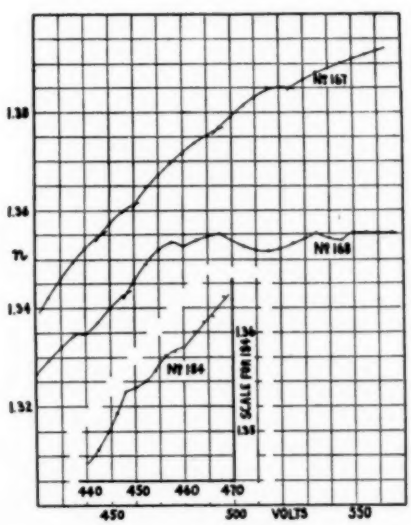


Fig. 11. Secondary emission curve of tungsten, primary velocity range of 420 to 570 volts. No. 167, $T=1270°K$, $e_A=V+200$ volts, $e_C=+10$ volts; No. 168, cold, $e_A=V+200$ volts, $e_A=+10$ volts; No. 184, $T=1350°K$, $e_A=V+200$ volts, $e_C=+10$ volts.

velocities, and the variation becomes considerable above 200 volts velocity. For low velocities the variation of n during a run is hardly measurable. The effect of adsorption of gases should not have any influence on the position of

breaks, as the galvanometer readings were taken at equal time intervals, nor should any new changes of slope be produced through the variation of n.

The relative decrease of n between 16 and 22 volts, Fig. 5, becomes smaller with rising temperature. With cold tungsten the maximum at 16 volts is considerably more marked. Curve No. 138 of Fig. 5, which was taken with a retarding potential of 4 volts between C and the target, shows a greater decrease of n between 16 and 22 volts than there is with a positive collecting potential as shown in curve No. 135. Apparently the maximum is due to a decrease in reflection of the primary electrons above 16 volts. It is known through other observations[3,4] that at primary velocities of a few volts a large proportion of the secondary emission consists of reflected electrons.

While the large changes of slope between 60 and 70 volts are easy to measure, the details of this region are not always reproducible. Curves like

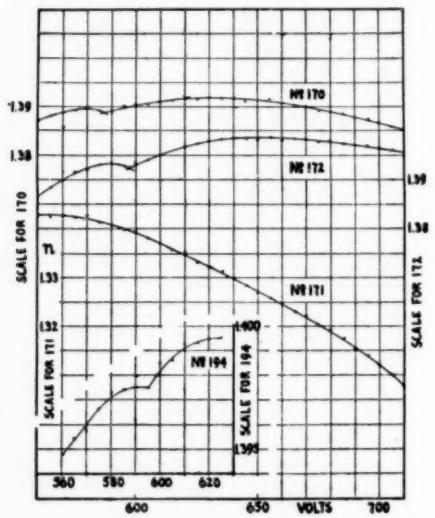


Fig. 12. Secondary emission curve of tungsten, primary velocity range of 560 to 710 volts. No. 170, $T=1270°K$, $e_A=V+200$ volts, $e_C=+10$ volts; No. 172, $T=1410°K$, $e_A=V+200$ volts, $e_C=+10$ volts; No. 171, cold, $e_A=V+200$ volts, $e_C=+10$ volts; No. 194, $T=1270°K$, $e_A=V+200$ volts, $e_C=+10$ volts.

No. 196, Fig. 7, are always obtained with hot tungsten, when the primary velocity is varied in large steps. There are two breaks at 62 and 71 volts. If the primary velocity is varied in smaller steps, curves like No. 126, 148, and 150 are obtained. With cold tungsten the following breaks appear: 55, 58, 63, 68, 72.5 and 76 volts. However, with a very hot, well degassed target we have: 55, 62, 66, 70.5 and 76 volts. If the target is not sufficiently well degassed, both kinds of breaks appear even at higher temperatures. Between 57 and 68 volts the curve of cold tungsten (No. 150) is rather different from that of hot tungsten. The break at 56 volts is generally not observed with hot tungsten. The four values between 60 and 75 volts given in

[4] A. Becker, Ann. d. Phys., **78**, 253 (1925).

Table II were obtained from three runs taken at temperatures above 1400°K. The breaks measured with cold tungsten are possibly due to adsorbed gases.

No breaks appear on curve No. 130, Fig. 7, which was taken after the tube had been standing without liquid air for a few days. The target was not heated prior to this run, the surface, therefore, was covered with a comparatively large amount of gas. This curve is very similar to the one measured by Petry, the values of n being about the same. The disappearance of the breaks when much gas is on the metal quite evidently explains the negative result of Petry.

Up to 475 volts primary velocity the curve taken with cold tungsten, No. 168, Fig. 11, is very similar to that of hot tungsten. Above this velocity the two curves have an entirely different shape, the difference starting very abruptly at 475 volts. The considerable decay of the curve taken with cold tungsten, No. 171, Fig. 12, is not due to such a variation of n with the primary velocity, but is caused by adsorption of gases, producing a decrease of n with time. After a sufficient length of time which depends on the degree of vacuum, n becomes constant, because of some equilibrium being established. Measurements carried out with target No. II in this condition put the maximum of the secondary emission curve at 620 volts with $n=1.28$ instead of 1.40 for the same target when hot. This value of n for cold tungsten is, of course, an accidental one, as n is reduced further if an additional clean-up of gas by the metal is made possible. The shape of curve No. 168, Fig. 11, however, cannot be explained by the variation of n with time, as the points of this curve were determined at equal intervals of time.

6. Other Measurements of the Secondary Emission Curve

While in previous investigations the secondary emission curve of a metal was found to have inflections or maxima and minima at a primary velocity of a few volts, breaks above 20 volts velocity have been reported only by Petry and by Stuhlman.[5] With tungsten Petry[2] obtains breaks at 20.2, 24.3, 35.5, 41.0, 84.5 and 266.5 volts. Trying to identify these breaks with some of those found in the present investigation seems to be rather uncertain. The fact that Petry does not observe the maximum at 16 volts and the large change of slope at 65 volts suggests that the breaks he found are quite different from the ones measured in this case.

7. Breaks in the Soft X-Radiation of Tungsten

The soft x-radiation of tungsten has been studied by Richardson and Chalklin,[6] Boyce,[7] and Bazzoni and Chu.[8] In Table II the critical velocities in volts found by Richardson and Chalklin are given. When comparing breaks found in the secondary emission curve with those of the soft x-radiation, the different role of the work function of the target has to be considered.

[5] O. Stuhlmann, Phys. Rev., **25**, 234 (1925).
[6] O. W. Richardson and F. C. Chalklin, Proc. Roy. Soc., **110**, 247 (1926).
[7] J. C. Boyce, Phys. Rev., **23**, 575 (1924).
[8] C. B. Bazzoni and C. T. Chu, J. Frank. Inst., **197**, 183 (1924).

Besides other corrections, the work function Φ of the target has to be added to the voltage, V, of a break in the soft x-radiation, in order to obtain the true value of the critical potential corresponding to the break, V being the voltage applied between the cathode and the target. In case of secondary emission, however, the primary electron has to have an excess of at least Φ over the critical potential, in order to be able to get out of the metal, or to communicate to the ionization electron, the energy required for overcoming the work function. Therefore, the voltage applied between the cathode and the target, corrected on account of voltage drop of the cathode, initial velocity and contact potential, is equal to the critical potential, in case of secondary emission. The values of Richardson and Chalklin, not corrected on account of work function, agree better with the breaks of the secondary emission curve than the corrected ones except for the breaks near 110 and 128 volts. This holds especially for the three lowest breaks. Both Boyce and Bazzoni and Chu found critical potentials between 30 and 40 volts and one near 70 volts. Boyce also reports breaks at 360, 403 and 583 volts.

8. Computed N and O-Energy Levels of Tungsten

Considering the good agreement between soft x-radiation and secondary emission, a comparison of the breaks found in the secondary emission curve with computed energy levels of tungsten may be expected to give a possible explanation of the origin of some of the breaks.

In Table II the fifth column gives ν/R-values of 18 critical potentials of the secondary emission curve measured with hot tungsten. In the last two columns the values for the N and O-energy levels of tungsten are shown as computed by Bohr and Coster[9] and by Nishina.[10]

At the present stage, no definite interpretation of the breaks can be made by a mere comparison between computed energy levels and the breaks. Identification of the breaks corresponding to the N and O-levels will more likely be possible in connection with measurements on metals near tungsten, when the relation between ν/R values and atomic number may be followed up. Under such circumstances it is probable that an explanation for the other breaks will be found too. Considering the agreement in Table II, however, the assumption appears to be justified that some of the breaks in the secondary emission curve are due to energy levels of tungsten.

9. Influence of Adsorbed Gases

The influence of adsorption of gases on the secondary emission curve was followed up systematically in the range of 10 to 30 volts.

The curves shown in Fig. 13 are taken with different amounts of gas on the tungsten, the amount of gas increasing the higher the position of the curves in the drawing. The adsorbed gases are produced by the discharge in the tube. Shortly after heating, as shown by curve No. 139, there is a small maximum instead of the inflection existing in case of hot tungsten (cf. Curve

[9] N. Bohr and D. Coster, ZS. f. Physik, **12**, 342 (1923).
[10] Y. Nishina, Phil. Mag., **49**, 521 (1925).

No. 135, Fig. 5). With more gas on the target this maximum increases rapidly while the maximum at 16 volts decreases. Finally, a curve like No. 176 is obtained. However, if the target is allowed to take on much more gas, all these maxima and minima disappear. Curve No. 131 was taken under such conditions.

The exact potentials of the two maxima are 16.5 and 12.5 volts, or on account of the usual correction, 15.5 and 11.5 volts.

This behavior of the secondary emission curve is undoubtedly due to the adsorption of gases. There is perhaps some relation between the maxima and critical potentials of such gases.

As is well known from the work of Langmuir there exists on the surface of tungsten a layer of adsorbed oxygen which cannot be removed by heating

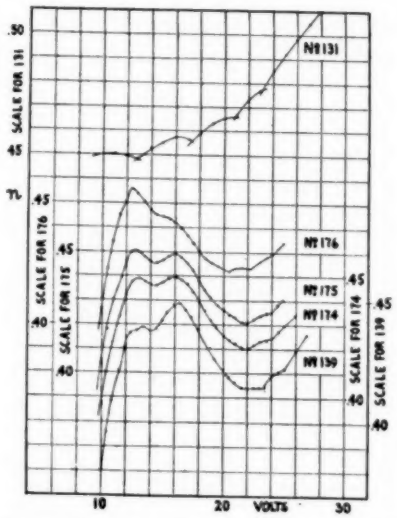


Fig. 13. Cold tungsten, effect of adsorption of gas on shape of secondary emission curve for primary velocity range of 10 to 25 volts. $e_A = V + 100$ volts, $e_G = +1$ volt; No. 139, $\frac{1}{2}$ hour after heating; No. 174, larger amount of gas adsorbed; No. 175, shortly after No. 174; No. 176, amount of gas adsorbed larger than with No. 175; No. 131, after one week without liquid air on charcoal.

below 1600°K. The maximum at 15.5 volts corresponds perhaps to the ionization potential of the oxygen molecule. The phenomena due to further adsorption are difficult to explain. One possible explanation is that the maximum at 11.5 volts is due to the hydrogen molecule which, in some way, causes the effect due to oxygen to disappear. The potential of the maxima may not be measured correctly, as the contact potential between the target and the cathode might vary in the course of the clean-up process.

The break near 39 volts, Fig. 6, which was found to be intermediate in strength with hot tungsten does not exist with the tungsten in the condition of curve No. 176, where the maximum at 15.5 volts has almost disappeared, while the two inflections at 29.5 and 33 volts are not affected. Perhaps the break near 39 volts is also due to the oxygen layer.

It is made rather probable through curve No. 138, Fig. 5, where all electrons having velocities less than 4 volts are kept back on the target, on account of a retarding field on C, that the form of the secondary emission curve in this low velocity range is mainly due to the laws of reflection of the primary electrons. According to this assumption, reflection decreases considerably above 15.5 volts.

The differences between the curves taken with hot and cold tungsten near 56 and 475 volts are probably due to adsorbed oxygen. Mohler and Foote[11] found 478 volts for the K-level of oxygen. Values given by Robinson[12] and Kurth[13] are 497 and 519 volts. Kurth also gives 50 volts for the L-levels. The measurements of Robinson and of Kurth were carried out with compounds of oxygen.

The maximum and the minimum in the range of 10 to 25 volts entirely disappear, if much gas is taken on by the target. Curve No. 131, which is similar to the one measured by Petry, was taken under such conditions.

10. Conditions for the Appearance of Breaks

The breaks appearing in the secondary emission curve of hot tungsten are also obtained with cold metal as long as it has not been able to pick up much gas. Evidently, the influence of temperature consists mainly in the removal of gases from the metal. With cold tungsten, shortly after heating, a few more breaks are found than with hot tungsten. Some breaks are probably caused by adsorbed gases. Up to 1500°K tungsten is not entirely free from adsorbed gases. If the metal gets beyond a certain stage in the adsorption of gases, no breaks are found. This fact explains why the numerous breaks measured in this investigation were not found by other observers. The changes of slope in the range of a few volts are probably due to adsorbed gases.

In spite of the large number of observations made, it cannot be decided at present whether there is a direct influence of temperature on the degree of secondary emission. If there is such an influence, it can be only small. This question will be further investigated through special measurements which will be carried out as soon as possible.

Research Laboratory,
Incandescent Lamp Department
General Electric Company,
Cleveland, Ohio.
August, 1927.

[11] F. L. Mohler and P. D. Foote, Bur. Standards Sci. Papers, No. 425 (1922).
[12] H. Robinson, Phil. Mag., **50**, 241 (1925).
[13] E. H. Kurth, Phys. Rev., **18**, 461 (1921).

THE MAGNETIC ANALYSIS OF A LUMINOUS CANAL RAY BEAM IN HYDROGEN

By Charles J. Brasefield*

Abstract

A method is described for splitting a luminous canal ray beam in hydrogen into its four component parts, namely the neutral, H_2^+, H^+ and H_{2-1}^+ beams, by applying a transverse magnetic field. From the variation in intensity of the H_2^+ and H_{2-1}^+ beams with pressure, the *free path for dissociation* into H_{2-1}^+ of a 1000 volt H_2^+ ion is found to be 0.37 cm at a pressure of 0.01 mm, which is about one-fourth the kinetic theory value for the mean free path of a neutal hydrogen molecule. Also the ratio of the light emitted per centimeter path by an atomic ion to that emitted by a molecular ion is found to be one-fifth.

Introduction

THE effect of a magnetic field on a beam of positive rays is a well known phenomenon. It has been studied by observing the photographic effect produced when the ions impinge on a fluorescent screen, the variation in the heating effect as they impinge on a thermo-junction and the variation in the rate of charging of some collector. But to the writer's knowledge, no one has ever observed any appreciable effect of a magnetic field on the luminous canal ray beam itself.

In the volume of the "Handbuch der Experimental-Physik" devoted to "Kanalstrahlen" under "Magnetische Ablenkung," Wien mentions only his own experiment in which he found a slight displacement of the spot on a fluorescent screen when a magnetic field was applied. G. P. Thomson[1] tried to analyse a narrow luminous pencil of positive rays by magnetic and electric fields in the ordinary manner but found the light obtainable from a pencil sufficiently small to give sharp resolution was totally inadequate for spectroscopic investigation. Similarly Baerwald[2] was unable to deflect more than an inappreciable part of the intensity from a canal ray beam. By using an experimental arrangement quite similar to one which had previously been successfully used by A. J. Dempster,[3] the writer was able to split a luminous beam of slow hydrogen canal rays into its component parts by applying a transverse magnetic field.

Apparatus and Procedure

The experimental arrangement used to produce the canal rays is shown in Fig. 1. *A* is the anode, a small cylinder of sheet nickel closed at one end.

* National Research Fellow.

[1] G. P. Thomson, Phil. Mag. **40,** 240 (1920).

[2] Baerwald, Ann. d. Physik **34,** 883 (1911).

[3] A. J. Dempster, Phys. Rev. **8,** 651 (1916).

F is an oxide-coated strip filament, mounted on the same stem as A and removable by means of a ground glass joint. C is a hollow cylinder of Swedish iron which serves both as a cathode and a magnetic shield for the discharge. The pole pieces M are also of Swedish iron and are separated by the walls of the tube from the pole pieces of an electromagnet. F, C, and M are all at the same potential while the potential of A is approximately 1000 volts.

Hydrogen is generated by electrolysis of barium hydroxide; then passed over platinized asbestos heated to 300°C which removes traces of oxygen; then over phosphorus pentoxide which removes water vapor; and finally into a large reservoir. From the reservoir it is admitted to the system through an artificial leak so chosen that one atmosphere pressure in the reservoir gives the maximum desired pressure in the system. After passing through a liquid air trap, the hydrogen enters the tube to the right of C and is pumped out above M by a high speed mercury diffusion pump. Thus a constant stream of pure hydrogen passes through the apparatus. Gas pressures are measured by means of a McLeod gauge.

Electrons emitted from the filament F are accelerated towards A and produce positive ions by collision with neutral molecules. These positive

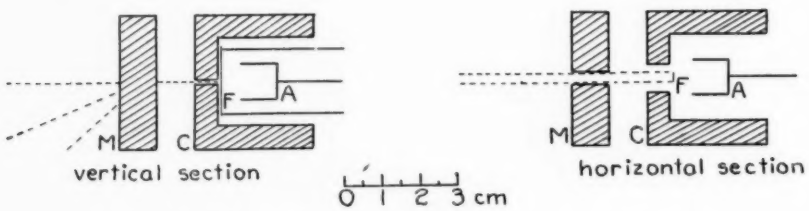


Fig. 1. Apparatus used to produce 1000 volt canal rays in hydrogen.

ions are accelerated in the reverse direction to the filament F (the homogeneous velocity of the positive ions indicates that the whole potential drop occurs in a region very close to F). Passing F on either side, the positive ions emerge through the slit in C and come under the influence of the magnetic field at M where they are deflected according to their momenta. Under favorable pressure conditions, the canal ray beam is actually split into four parts when the magnetic field is applied. One of these parts is undeflectable and thus is composed of neutral particles. The other three parts are deflected by the magnetic field and from their angles of deflection it can be shown that they are due to the charged ions H_2^+, H^+ and H_{2-1}^+, that is, an ion that came through the electric field as H_2^+ but which dissociated into H^+ before reaching the magnetic field.

As the pressure is reduced, the phenomena which are observed are as follows. At pressures above 0.025 mm it is impossible to obtain any deflected beam, the whole canal ray beam being composed of neutral particles. At 0.025 mm, a very weak beam can be deflected which is due to H_{2-1}^+. As the pressure is lowered, the neutral beam becomes weaker and the H_{2-1}^+ beam stronger. At 0.007 mm, another weak beam appears between the neutral

and H_{2-1}^+ beams which is due to H_2^+ (see Fig. 2a). As the pressure is lowered still further, the neutral and H_{2-1}^+ beams become weaker and the H_2^+ beam stronger. At 0.004 mm, the neutral beam is hardly visible while the H_2^+ and H_{2-1}^+ beams are of equal intensity (see Fig. 2b). As the pressure is lowered further, the neutral beam dies out and at 0.0025 mm the H_{2-1}^+ beam is barely visible (see Fig. 2c). Below this pressure all the particles in the canal ray beam are H_2^+ ions.

It is of interest to observe that on the photograph in Fig. 2b, there appears a very faint beam between the H_2^+ and H_{2-1}^+ beams, which is evidently due to H_1^+, that is, to atomic ions which were accelerated through the electric

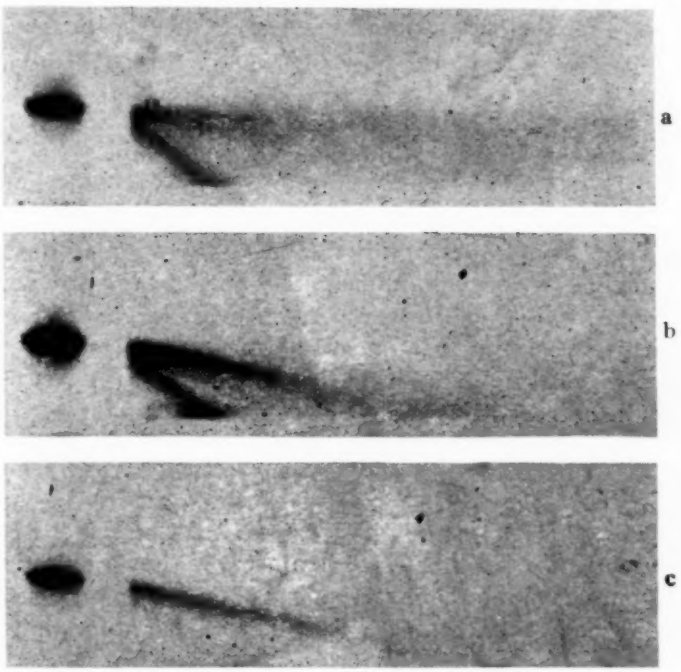


Fig. 2. Photographs of a 1000 volt canal ray beam in hydrogen deflected by a magnetic field (a) at 0.007 mm, (b) at 0.004 mm, (c) at 0.0025 mm pressure.

field as H^+. This beam was too weak to be observed visually, and was not detectable in any photographs at pressures either higher or lower than 0.004 mm.

Discussion

It has been shown above how the intensities of the H_2^+ and H_{2-1}^+ beams vary with the pressure. From a study of the variation of these intensities with pressure and the fact that the H_{2-1}^+ ions are the disintegration products of the H_2^+ ions, it is quite easy to determine the free path of the H_2^+ ion before it dissociates into H_{2-1}^+, as well as the ratio of the light emitted by an atomic ion per centimeter path to that emitted by a molecular ion.

If $e^{-x/\lambda}$ is the probability that the H_2^+ ion goes a distance x without changing to H_{2-1}^+ and N_0 the number of H_2^+ ions leaving F, then the number of H_2^+ ions which go a distance x unchanged is $N_0 e^{-x/\lambda}$ and the number of H_2^+ ions that are changed to H^+ in a distance x is $N_0(1-e^{-x/\lambda})$. In the experiment the distance x from F to the near edge of M was 1.7 cms, so that $N_0 e^{-1.7/\lambda}$ molecular ions and $N_0(1-e^{-1.7/\lambda})$ atomic ions are deflected by the magnetic field into the two corresponding canal ray beams.[4]

The intensity of light observed in either beam is proportional to the number of particles in the beam and to the pressure of gas, that is, to αpN, where α may be different for each ion. If y is the ratio of the intensity of the H_{2-1}^+ to the H_2^+ beams at pressure p, then $y=C(e^{1.7/\lambda}-1)$, where $C=\alpha_1/\alpha_2$. Let λ_0 be the free path of the H_2^+ ion at 0.01 mm pressure. Then

$$y=C(e^{170p/\lambda_0}-1) \tag{1}$$

To determine y, the light of the beams was compared with the light from a blue daylight lamp as diffused by a milk glass plate and filtered through blue glass to give the appropriate color. The light from the lamp served as a background for comparison with the canal ray beams, the current through the lamp being varied until the background was as intense as the beam (of course the background immediately behind the beam was cut out). Thus observations were made on both beams over a large range of pressures. Then the lamp was calibrated by means of a Lummer-Brodhun photometer and the values of y calculated.

If C is small compared to y, we get as a first approximation

$$y=C_1 e^{170p/\lambda_0} \tag{2}$$

or

$$\log_e y=\log_e C_1+170p/\lambda_0$$

The curve obtained by plotting $\log_e y$ against p is shown as the dotted line in Fig. 3. From the y intercept we get $\log_e C_1=-1.96$ or $C_1=0.14$. Substituting this value back in Eq. (1) we get as a second approximation

$$y+C_1=C_2 e^{170p/\lambda_0} \tag{3}$$

or

$$\log_e (y+C_1)=\log_e C_2+170p/\lambda_0$$

The curve obtained by plotting $\log_e (y+C_1)$ against p is shown as the solid line in Fig. 3. From the slope of this curve we get $\lambda_0=0.37$ cm and from the y-intercept $C_2=0.20$. Further approximations do not alter these values appreciably.

Thus we now have the free path of a 1000 volt H_2^+ ion before it dissociates into H_{2-1}^+ is 0.37 cm at a pressure of 0.01 mm.[5] The kinetic theory

[4] The chance of neutralization of an H_2^+ ion is evidently small or a Doppler effect would be observed in the secondary spectrum of hydrogen. The free path of the H^+ ion for neutralization is assumed very large compared with λ for canal rays of this velocity. See A. J. Dempster, Proc. Nat. Acad. Sci. **11**, 552 (1925).

[5] Experiments indicate that the free path of the H_2^+ ion is independent of the velocity of the ion, at least between 100 and 1000 volts.

value for the mean free path of a hydrogen molecule is 1.39 cm at 0.01 mm pressure. Hence the free path for dissociation of a 1000 volt H_2^+ ion is about one-fourth the kinetic theory value for the molecule. It is of interest to note that Smyth has assumed the free path of H_2^+ is one-fifteenth the kinetic theory value.

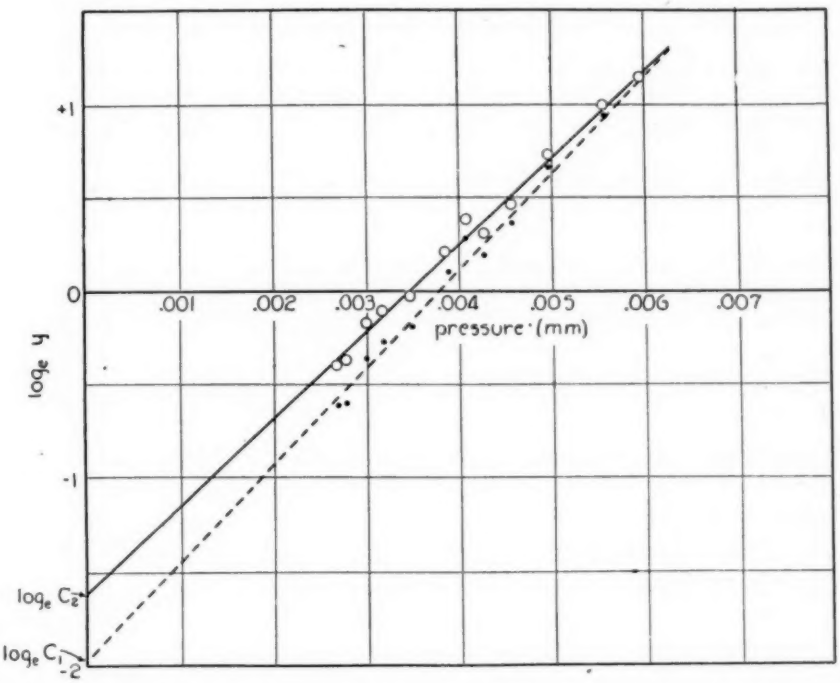


Fig. 3. The slope of the solid curve gives the value of λ_0 and the y-intercept the value of C.

From the value of C_2 we conclude that the ratio of the light emitted per centimeter path by an atomic ion to that emitted by a molecular ion is one-fifth. Or, the path of the H^+ ion for light excitation is five times that of the H_2^+ ion if we assume that the same amount of light is emitted by each ion at a collision.

A study is now being made of the spectra emitted by the various beams. The writer is deeply indebted to Professor A. J. Dempster for many helpful suggestions.

RYERSON PHYSICAL LABORATORY,
UNIVERSITY OF CHICAGO.
November 8, 1927.

NOTE ON THE ROLE OF POSITIVE IONS IN THE DISRUPTIVE DISCHARGE

By J. S. Townsend

IN A recent paper by W. J. Jackson[1] the following statement is made: "In a paper criticizing the theory of sparking based on secondary emission as set forth by Holst and Osterhuis, Townsend rejects all modes of generation ions as contributing to the effect required to explain the disruptive discharge save the method which assumes the extra ionization as due to the collisions of positive ions with gas molecules."

I should like to call attention to the following passage which occurs in my paper to which Mr. Jackson refers: "The question then arises as to which of these modes of producing ions combined with the direct ionization by the collisions of electrons gives the most satisfactory explanation of the sparking potentials *when the pressure of the gas is above that corresponding to the minimum sparking potential*, and the small currents obtained with various distances between the electrodes when ultra-violet light falls on the negative electrode." Mr. Jackson omits to notice the importance of the words in italics.

May I also be permitted to make the following quotation from my book on "Electricity in Gases," published in 1915. In section 230 where the relative importance of the two effects, that of the positive ions in ionizing molecules of the gas, and that of positive ions in setting free electrons from the negative electrode is discussed, the following conclusion is arrived at. "The relative importance of the ions set free from the negative electrode increases as the pressure diminishes and when $a \times p$ is very small the ions generated in the gas by the positive ions are probably few in number compared with the number that are set free from the negative electrode.

There are no reliable experiments to show the relative values of these two effects in a discharge for a given value of the product $p \times S$ but for simplicity it may be assumed that the gas effect predominates when the product $p \times S$ exceeds the value corresponding to the minimum sparking potential.

It appears to me that Mr. Jackson's experiments confirm rather than disprove this conclusion.

Electrical Laboratory,
Oxford, England,
October 29, 1927.

[1] W. J. Jackson, Phys. Rev. **30**, 473 (1927).

THERMOELECTRIC PHENOMENA IN CRYSTALS AND GENERAL ELECTRICAL CONCEPTS

By P. W. Bridgman

Abstract

It is shown that when an electric current passes across an interface where the crystal orientation changes there is a Peltier heat, but no corresponding jump of potential. This demands that we analyze the action of an impressed e.m.f. into two aspects. The following definitions are suggested: (1) energy per unit time delivered by the source when current i flows $= i \times$ "working" e.m.f.; (2) $i =$ ("driving" e.m.f. $-\Delta V$) $/\Delta R$. In ordinary isotropic materials this analysis is not necessary, but it is necessary in unequally heated materials in which thermal currents are flowing. In an unequally heated metal the "driving" e.m.f. between two points at a temperature difference $d\tau$ is $-d\tau\int_0^\tau \sigma d\tau/\tau$, and the "working" e.m.f. between the same two points is $\sigma d\tau$. It is shown that these expressions demand that the current convect with it the energy $\tau\int_0^\tau \sigma d\tau/\tau$, which must be described as thermal energy. We are able in these terms to give a thermodynamically consistent account of the energy transformations in all parts of a thermo-electric circuit. The theoretical significance of a thermal energy which depends on the direction of current flow is emphasized. The argument may be extended from crystals to ordinary isotropic substances. A number of questions peculiar to crystals are discussed. The existence of an internal Peltier heat when the direction of current flow changes is proved, and the importance of this effect for all theories of conduction is emphasized. Some fine structure seems demanded in a metal which is not ordinarily taken into account. Equipartition cannot hold, but the thermal energy of the electrons is of the same order of magnitude as that given by equipartition. Formulas are derived for the internal Peltier heat as a function of the direction of current flow, for the surface heats and for the two latent heats of evaporation of electrons. The possible existence of a Volta difference of potential between different faces of the same crystal is recognized. An argument is drawn from the connection with the photo-electric effect suggesting that this Volta difference may possibly vanish.

IN THIS paper I propose to discuss the bearing of various thermo-electric phenomena in crystals on the problem of understanding thermo-electric action, and the even broader problem of the electrical behavior of metallic conductors in general. These phenomena in crystals bear both on our idea of the underlying mechanism, and on the very concepts in terms of which such electric phenomena are described.

All the conclusions of this paper can be obtained by the use of simple thermodynamics, in conjunction with certain exceedingly simple physical assumptions, and the fundamental experimental fact that the thermo-electric properties of a single crystal are in general different in different directions.

Imagine a thermocouple, in which one branch is a straight rod cut from a single crystal in a definite orientation, and the second branch is some isotropic metal, such for example, as copper, as shown in Fig. 1. When the junctions are brought to different temperatures this couple functions exactly as any ordinary couple. A current flows in the circuit; the source of the energy

which drives this current is heat, which flows into the circuit at the two junction points as Peltier heat, and into the parts of the circuit where there is a temperature gradient as Thomson heat. We assume these heats to be reversible, and thermodynamics to be applicable to the system, as in the ordinary analysis. Then if for the sake of definiteness we suppose the crystal rod cut parallel to the axis, we have the relations

$$P_{\parallel Cu} = \tau d E_{\parallel Cu}/d\tau$$

$$\sigma_{Cu} - \sigma_{\parallel} = \tau d^2 E_{\parallel Cu}/d\tau^2$$

for the Peltier and the Thomson heats respectively. $E_{\parallel Cu}$ is the total e.m.f. of the couple, between a fixed lower and a variable upper temperature, directed from $\parallel$ to Cu at the hot junction.

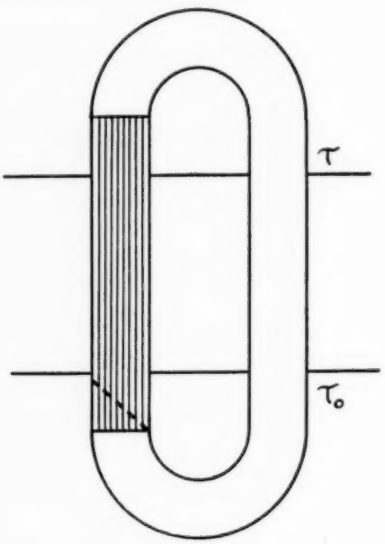


Fig. 1.

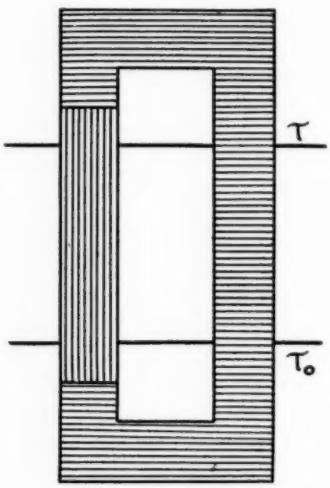


Fig. 2.

We may now construct another similar thermocouple, with the rod cut perpendicular to the axis, and obtain a similar set of formulas. Then by subtracting one set of formulas from the other, and using the relations $P_{\parallel Cu} - P_{\perp Cu} = P_{\parallel\perp}$ etc., which are valid for ordinary thermocouples, and are also valid here, since they follow immediately from the impossibility of obtaining work from a complete cycle at constant temperature, we have the equations:

$$P_{\parallel\perp} = \tau d E_{\parallel\perp}/d\tau \qquad \text{(I)}$$

$$\sigma_{\perp} - \sigma_{\parallel} = \tau d^2 E_{\parallel\perp}/d\tau^2, \qquad \text{(II)}$$

which apply to a couple, the two branches of which are cut from the same crystal, but have different orientations, as shown in Fig. 2. These formulas are in all respects like the formulas which apply to a couple composed of two

different isotropic metals. It is furthermore obvious that similar formulas apply to rods cut from the crystal in any two directions.

There is, then, a Peltier heat when current flows across the surface separating two parts of the same crystal turned so as to have different orientations. As we have drawn it, the surface at which Peltier heat is absorbed is perpendicular to the direction of current flow, but there is no necessity in this restriction, for it is obvious in Fig. 1 that the surface of separation of the crystal from the copper might have been inclined at any angle to the direction of current flow, as shown by the dotted line, with no change in the total heat absorbed, because of the thermodynamic fact that no rearrangements of the parts of the circuit at constant temperature can have any net effect. The Peltier heat at the surface of a crystal depends, therefore, on the direction of flow of the current with respect to the crystal as it crosses the surface, and not on the orientation of the surface itself with respect to the crystal.

What physical account shall we now give of the nature of the action at the surface where this absorption of heat takes place? In the case of the ordinary thermocouple between isotropic metals there is more or less common consent as to the method of picturing the phenomenon. We recognize that there are two entirely different sorts of action at the surface. One of these is connected with the Volta difference of potential. This Volta difference, which as given by experiment is a difference between points outside the metals, may be divided in various ways between three surfaces, two separating the metals from surrounding empty space, and one separating the two metals from each other. There is not yet any agreement as to how this division should be made. But entirely apart from the Volta phenomenon, and of an order of magnitude only one one-hundredth as large, there are the surface effects responsible for the Peltier heat. We think of the surface of separation of the two metals as the seat of an impressed e.m.f., which functions in the two distinctly different ways that all ordinary e.m.f.'s do. The first function of the impressed e.m.f. is to deliver energy to the current as it flows across the junction in amount precisely equal to the Peltier heat. The second function is to tend to produce a motion of electricity, that is, to produce a current, precisely like an ordinary electric force. But now Ohm's law applies in the surface of separation, so that unless there is a finite resistance in an infinitesimal thickness at the surface, the impressed e.m.f. acting in this way would give an infinite current. This can be avoided only by supposing the development of a precisely equal opposing jump of electrostatic potential. But a jump of potential demands, by the ordinary laws of electrostatics, a double layer at the surface. The strength of this double layer must be equivalent to the Peltier heat. The electrostatic potential with which we are concerned here is the ordinary electrostatic potential of elementary macroscopic theory; it is a smooth point function, to be calculated by the law of the inverse first power from the position of distant electric charges. It is also to be noticed that we are restricting ourselves to steady systems.

The impressed e.m.f. which the conventional mode of representation employs to picture the action at a junction where there is a Peltier heat is

exactly similar in its properties to the ordinary body forces of electrostatics, differing from such body forces only in the unknown nature of its origin. This impressed e.m.f. delivers energy when a current moves with it in amount equal to the product of current and e.m.f., and of itself tends to produce a current. The expression of Ohm's law in a substance where there is such action is: $i = (\text{e.m.f.} - \Delta V)/\Delta R$, where the e.m.f. of the equation is the total e.m.f. acting between two points whose difference of electrostatic potential is ΔV, and ΔR is the resistance between the same two points. This view of the nature of an impressed e.m.f. will be found explicitly stated, for example, in Abraham's treatment of the field equations.

Although this picture of an impressed e.m.f. functioning in these two ways (delivering energy and entering Ohm's law) is the usual one, it is by no means necessary, and in fact cases are already known in which this account of the nature of the action on a current in not broad enough to correspond to the physical phenomena. In particular, in an electron gas, in which there is an ordinary gas pressure, the conventional account of the situation fails. I have already discussed this matter at some length,[1] and from the fact that the ordinary account is demonstrably inadequate in an electron gas have drawn the conclusion that in general in a metal we must keep distinct these two possible aspects of the action on electricity. I insisted, in particular, that at a junction we could not equate Peltier heat, impressed e.m.f., and potential jump. I gave formulas in which these three things were explicitly recognized as different, but at the time was not able to go further in definitely splitting the action into its different aspects. One of the chief points of this paper is that phenomena in crystals give us a method of taking the next step, and of definitely specifying the relation between these different aspects of the action.

We are able to effect this analysis because we are able to show that in a crystal there can be no jump of potential at a surface where the orientation changes. Fig. 3 represents two pieces of the same crystal, differently oriented with the circuit completed by an isotropic metal. The system is at constant temperature, with no current flowing, and is therefore in equilbrium. Now describe the path indicated from A to B. There can be no changes of potential inside the homogenous metal, either crystal or isotropic, so that the only possibilities of a variation of potential in the path are at the two surfaces of discontinuity, at C and D. But these two surfaces of discontinuity are identical, so that if we make the simple and almost unavoidable assumption that any jump of potential at a surface of discontinuity is determined merely by local conditions at the surface, we see that any change of potential encountered at the surface C is wiped out at the surface D, which is traversed in the opposite direction, and therefore there can be no difference of potential A and B. The same conclusion is forced from an examination of the compound crystal shown in Fig. 4. If there can be no potential change inside the body of homogeneous metal and if the potential jump at a surface depends

[1] P. W. Bridgman, Phys. Rev. **14**, 306–347 (1919).

only on the relative orientation of the abutting parts, then the potential at B exceeds that at A by the same amount that the potential at C exceeds that at D, and if the potential at B is equal to that at D, and that at A is equal to that at C the potential throughout the entire interior of the compound system must be the same, and there can be no jump at an interface.

We appear driven, therefore, to the conclusion that at a surface of discontinuity of orientation there can be no jump of potential, and therefore no double layer. *The impressed action at an interface is such as to deliver energy to the current, but it does not enter Ohm's law, and it does not tend to produce a current.*

Can we now extend these conclusions to the other parts of the circuit, and say that the action which we usually describe in terms of a Thomson e.m.f. involves only a transfer of energy to the current equal in amount to the

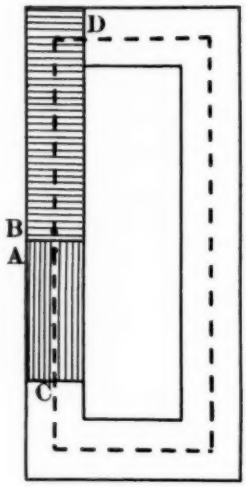


Fig. 3.

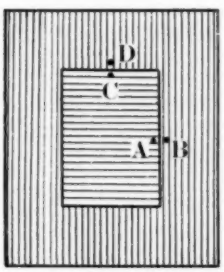


Fig. 4.

Thomson heat, but that this action involves no tendency toward the production of current? It is evident that we cannot make this extension, because a current flows in the complete thermo-electric circuit, so that somewhere in the circuit there must be something tending to set the current in motion. Furthermore, the net effect around the circuit, or the line integral of the tendency, must be the same as that given by the conventional analysis, because the conventional analysis gives the correct total flow. But is this possible; is it possible to locate in the *body* of the metal a driving e.m.f. such as to satisfy the integral condition?

Before we carry this discussion further it will be convenient to invent a notation that explicitly recognizes the two aspects of impressed action. In lack of anything better, I shall speak of an impressed "working" e.m.f., $(\text{e.m.f.})_w$, and an impressed driving e.m.f., $(\text{e.m.f.})_d$. These two quantities are defined through the equations:

1. Energy* per unit time delivered by the source when current i flows = $i \times (\text{e.m.f.})_w$

2. $$i = [(\text{e.m.f.})_d - \Delta V]/\Delta R \qquad \text{(Ohm's law)},$$

where ΔR is the resistance between two points whose difference of potential is ΔV.

We are now required so to locate a driving e.m.f. in the body of the metal that there is the proper net effect in the complete thermo-electric circuit. This may be accomplished by integrating the equations connecting the Thomson heat with the second derivative of the total e.m.f. We have

$$\frac{d^2E_{\parallel\perp}}{d\tau^2} = \frac{\sigma_\perp}{\tau} - \frac{\sigma_\parallel}{\tau}.$$

Integrating once,

$$\frac{dE_{\parallel\perp}}{d\tau} = \int_{\tau_0}^{\tau} \frac{\sigma_\perp}{\tau} d\tau - \int_{\tau_0}^{\tau} \frac{\sigma_\parallel}{\tau} d\tau + \text{const.}$$

In virtue of the condition on the Peltier heat

$$\text{const.} = (dE_{\parallel\perp}/d\tau)_{\tau=\tau_0} = (P_{\parallel\perp}/\tau)_{\tau=\tau_0}$$

Now if we put $\tau_0 = 0°$ Abs, $(P_{\parallel\perp}/\tau)_{\tau=0} = 0$, in virtue of the third law, which states that there can be no entropy changes at 0° Abs. This gives

$$dE_{\parallel\perp}/d\tau = \int_0^{\tau} \sigma_\perp d\tau/\tau - \int_0^{\tau} \sigma_\parallel d\tau/\tau, \qquad \text{(III)}$$

and integrating again

$$E_{\parallel\perp} = \int_0^{\tau} d\tau \int_0^{\tau} \sigma_\perp d\tau/\tau - \int_0^{\tau} d\tau \int_0^{\tau} \sigma_\parallel d\tau/\tau. \qquad \text{(IV)}$$

The constant of integration is here zero, because the total e.m.f. of a couple whose two junctions are at 0° Abs is zero. Now the form of the expression just obtained for E shows at once that the total e.m.f. may be obtained by assigning to each element of length reaching from τ to $\tau + d\tau$ a driving e.m.f. of amount $-d\tau \int_0^{\tau} \sigma d\tau/\tau$, driving the current in the direction of increasing temperature.

The working e.m.f. at various parts of the circuit is given by the conventional description, since this accounts consistently for the energy absorbed as heat by the system in the local parts of the circuit.

* In the following we do not speak of a current or an electron as having potential energy of position in the electric field, but when the mutual potential energy of the electron and the field changes we speak of a transfer of energy to the field by means of the Poynting vector. The electron or the current is from this point of view entirely neutral, constituting merely an intermediate link in a chain by which energy is transferred from some other agency to the field or vice versa. One can, if preferred, speak of the electron itself as having the potential energy, instead of the field; in this case the energy flow on the Poynting vector plays no part. These two points of view are really the same, and lead to the same formulas.

We now recapitulate the results found thus far. At a surface of discontinuity in the orientation there is an absorption of energy equal to the Peltier heat, and therefore by definition an equal working e.m.f., but there is no potential jump, no double layer, and no impressed driving e.m.f. In the body of the metal where there is a temperature gradient, there is an absorption of energy when current flows up the temperature gradient from τ to $\tau+d\tau$ of $\sigma d\tau$, that is, a working e.m.f. of $\sigma d\tau$, and there is furthermore between the same two points an impressed driving e.m.f. of $-d\tau\int_0^\tau \sigma d\tau/\tau$.

That we have been forced to recognize two different kinds of e.m.f. should not be disturbing, and in fact is to be expected as soon as we appreciate that the electronic structure of an electric current makes it in many respects like a current of an ordinary fluid. Consider, for example, an ordinary hot water circulating system. The source of the mechanical work used in overcoming the friction of the water against the pipes is thermal, but the current is *driven* by gravity, which can do no net work. The physical essence of our point of view is the recognition that there are other ways of imparting energy to electricity than by the action of a body force. This recognition is inevitable as soon as we discover the possibility of an electron gas which exerts a gas pressure and is the seat of thermal energy. That we have now been driven to recognize the existence of a similar situation inside a solid metal must be most significant for theories of metallic conduction.

Continuing with the argument, it is to be noted that the two e.m.f.'s which we have found in the body of the metal are, paradoxically, of opposite signs. It is evident, therefore, that this distribution of e.m.f.'s must involve a rather different description of the energy transformations in the circuit than the conventional one.

Before attempting a description of the energy transformations according to our new point of view, it will be well to have before us the conventional description of the situation. This description is suggested by Lord Kelvin's figurative ascription of a specific heat to the electric current. If we suppose that the current carries with it energy of amount $\sigma\tau$, or more generally $\int_0^\tau \sigma d\tau$, then we obviously have given a possible description of the absorption of Thomson heat. It is perhaps not generally recognized, however, that this method of associating thermal energy with the current is not consistent with the conventional views of the impressed e.m.f. We can see this in the following way. In an isotropic (non-crystalline) medium, in which a current is flowing, and in which there is a temperature gradient, consider the conditions of energy balance within any small closed surface. We can write the conditions of energy balance in two ways. First there is the geometrical condition on the closed surface, that no net energy cross the surface. Secondly, by regarding the current of electricity like a current of ordinary fluid, we have the condition that the energy carried by the current out of the region is equal to what it carries into the region, plus that acquired within. Suppose now that unit current convects with it the energy U. The first condition of energy balance, on the region, is

$$\text{div}\,(iU)+\text{div}\,(-k\,\text{grad}\,\tau)+i\cdot\text{grad}\,V=0 \qquad \text{(V)}$$

where the first term represents the net energy flowing out of the region carried by the current, the second term the energy flowing out as heat by conduction, and the third term the electromagnetic energy flowing out of the region on the Poynting vector. The second condition of energy balance, on the current, is

$$\text{div}\,(iU) = i\cdot\sigma\,\text{grad}\,\tau - i\cdot\text{grad}\,V - i^2\rho, \qquad \text{(VI)}$$

where the first term on the right hand side is the reversible heat absorbed by the current as Thomson heat, the second term is the energy given by the current to the field by means of the Poynting vector, and the third term is the Joulean heat imparted by the current to the matter occupying the region. If now the impressed action enters Ohm's law in the conventional way, we have also

$$i = (\sigma\,\text{grad}\,\tau - \text{grad}\,V)/\rho$$

Multiply this equation by $i\rho$, and substitute back in VI, obtaining $\text{div}\,(iU) = 0$. But since $\text{div}\,i = 0$, we must have $U = \text{Const}$, which is not the conventional expression of Kelvin for the convected energy.

The conventional points of view therefore contain an inconsistency. It is to be noticed that this inconsistency does not react on the equations by which σ is determined experimentally, for on eliminating $\text{div}\,(iU)$ between V and VI we get

$$i\cdot\sigma\,\text{grad}\,\tau = i^2\rho + \text{div}\,(k\,\text{grad}\,\tau),$$

which is the usual equation by which σ is determined from the distribution of temperature in an unequally heated bar carrying a current. (See, for example, Borelius.[2])

To what account of the energy transformations are we now driven by accepting the expression $-d\tau\int_0^\tau \sigma d\tau/\tau$ for the driving e.m.f. in a crystal? We write down an equation analagous to Equation (VI), but in order to avoid complications from a resistance which is a function of direction, we apply the condition to an element of length of a long slender linear conductor cut from a crystal in a definite direction. Taking the x axis along the length gives

$$\frac{\partial}{\partial x}(iU) = i\sigma\frac{\partial\tau}{\partial x} - i\frac{dV}{\partial x} - i^2\rho,$$

Ohm's law becomes

$$i\rho = -\frac{\partial\tau}{\partial x}\int_0^\tau \frac{\sigma}{\tau}d\tau - \frac{\partial V}{\partial x}.$$

Substituting back,

$$\frac{\partial}{\partial x}(iU) = i\frac{\partial U}{\partial x} = i\sigma\frac{\partial\tau}{\partial x} + i\frac{\partial\tau}{\partial x}\int_0^\tau \frac{\sigma}{\tau}d\tau = i\frac{\partial}{\partial x}\left[\tau\int_0^\tau \frac{\sigma}{\tau}d\tau\right].$$

[2] G. Borelius, Ann. d. Physik **56**, 388 (1918).

Integration of this equation gives, except for a constant which has no physical significance, $U=\tau\int_0^\tau \sigma d\tau/\tau$. *The condition of energy balance demands, therefore, that the current convect with it the energy* $U=\tau\int_0^\tau \sigma d\tau/\tau$. Since σ is a function of direction, the energy convected is also a function of direction.

What account does our new expression for convected energy give of the phenomena at surfaces of discontinuity? Assume for the sake of definiteness that the current flows from $\parallel$ to $\perp$. Then on crossing the surface there must be an absorption of energy equal to the difference of convected energy on the two sides of the surface, or

$$\tau\left[\int_0^\tau \sigma_\perp d\tau/\tau - \int_0^\tau \sigma_\parallel d\tau/\tau\right].$$

But this is exactly equal to $P_{\parallel\perp}$, as we see at once from equations I and III, and is as it should be if our picture is consistent.

What shall we suppose is the nature of the convected energy? It is not difficult to see that we must formally describe the convected energy as *thermal* energy. This means that at the junction the current absorbs thermal energy from its surroundings, and convects this away with it, still in thermal form, like water in a heating system. This is demanded by the account we have given of the driving and the working e.m.f.'s at the surface. For if there is no potential jump, there is no Poynting flow, and hence no conversion of thermal to electro-magnetic energy, and if there is no driving e.m.f. there can be nothing corresponding to a non-electrical difference of potential on the two sides of the surface, such as has been sometimes assumed in postulating a non-electrical potential energy of position of the electron inside the metal. Furthermore, we are enabled to give a correct description of the energy transformations in the unequally heated parts of the circuit by describing the convected energy as thermal. The requirement is that the fraction $d\tau/\tau$ (equal to $\partial\tau/\tau\partial x$ for unit length) of the thermal energy entering the region at the higher temperature be converted into non-thermal energy. The energy converted in unit length is the energy which flows out on the Poynting vector $(i\partial V/\partial x)$ plus the Joulean heat. Ohm's law already written, gives for the sum of these $i^2\rho+i\partial V/\partial x=-i(\partial\tau/\partial x)\int_0^\tau \sigma d\tau/\tau$. Now this is exactly equal to $(\partial\tau/\tau\partial x)$ $(-i\tau\int_0^\tau \sigma d\tau/\tau$, where the term in brackets is, to first order terms, equal to the energy convected into the region as heat by the current at the higher temperature, so that the thermodynamic requirement is completely met.

We have thus arrived at a consistent and definite method of describing the phenomena in a thermocouple consisting of two rods of the same crystal differently oriented, in which we have assigned definite and unequal values to working and driving e.m.f. at every point of the circuit, and have also found a unique value for the energy convected with the current, which we have had to describe as thermal energy. Can we not now give up the restriction that the results apply only to different orientations of the same crystal, and apply exactly similar expressions to couples composed of any two isotropic metals? It is at once evident that all the formulas do apply,

if we are satisfied merely with a possible solution. We might question, however, whether there might not be other solutions in this case, because our entire argument rested on the fundamental fact that there can be no jump of potential across a crystal interface, and there is apparently no corresponding relation at an interface between different isotropic metals. A little consideration shows, however, that we can make the desired transition from crystalline to isotropic metals by way of the expression for the convected energy. For in an isotropic metal, that is, a metal crystallizing in the cubic system, we must still have for the convected energy $\tau \int_0^\tau \sigma d\tau/\tau$, and must still describe this energy as thermal, as we can see by starting with a non-cubic lattice, in which these results always hold, and continually deforming the lattice until it becomes cubic. It follows that at an interface between two isotropic metals all the Peltier heat goes to increasing the thermal energy of the current, and that there can be no Poynting flow, and therefore no potential jump, nor any change of non-electrical potential energy of position. It follows that all our arguments and our explicit formulas for crystals at once apply to any isotropic metal.

It is significant that we have been driven to ascribe a *thermal* energy to the current. This would seem to prove that a theory of metallic conduction such as Wien's, which does not allow the motion of the electrons which constitute the current to be affected by temperature, cannot be correct. Recognizing, however, that the energy of the current must be thermal in character, we are confronted with the problem of understanding how this energy may be negative in some metals, as experiment shows it to be. A possible explanation is that the electrons, when moving in such a way as to constitute the current, may have greater or less energy of haphazard agitation than when they are not so moving, and that what we have called the thermal energy of the current is merely the difference of these two energies. In any case it no longer seems possible to suppose that the electrons have equipartition energy, although doubtless their energy may be of the same order of magnitude as that demanded by equipartition. This question will be referred to again in connection with the internal Peltier heat.

It is to be carefully noted that our energy considerations give no hold whatever on any Volta jump at the surface of discontinuity, for all the energy transformations involved in the Volta jumps are entirely electromagnetic in character, and thermodynamics has nothing to say about them. In the case of crystals, the first argument used above does apply, however, and there can be neither Volta nor Peltier jump at a surface of discontinuity in the crystal orientation.

We now turn from these more general matters to consideration of several questions peculiar to crystals. First we must emphasize a most important crystalline phenomenon, which I have already mentioned in previous papers. Consider the two thermocouples shown in Fig. 5 composed of crystal and isotropic metal. The total e.m.f. of these two couples is the same, because the only difference between the two systems is in the regions at constant temperature. Hence the total heat absorbed when unit quantity flows around

the circuit is the same in the two cases. Since the parts of the systems at temperature τ_0 are identical in the two cases, the heats absorbed in this part of the systems are the same. Hence the heat absorbed in the parts at τ must also be the same. Now in Fig. 5a, heat is absorbed at temperature τ only at the surface A. In Fig. 5b, heat is absorbed at A', but since the direction of current flow on leaving the surface A' is different from that at the surface A, this heat is not equal to that absorbed at A. Hence there must be some compensating absorption of heat somewhere else at temperature τ in Fig. 5b, and by the principle of sufficient reason, this can only be at the corner B where the direction of current flow changes. This I have called the internal Peltier heat. It is a heat per unit quantity of electricity, or per electron, and is therefore independent of the velocity with which the electron moves. The mere existence of this heat is a most significant thing. We have here an absorption of energy without change of position, and therefore without change of electrical potential, but merely a change of direction of motion. Since there is absorption of energy at the corner, we must recognize the existence of an

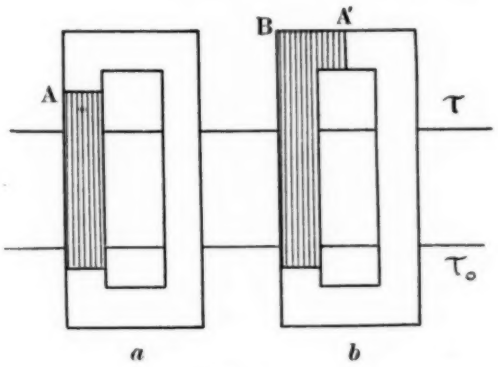


Fig. 5.

impressed working e.m.f., but since there is no change of potential, there can be no impressed driving e.m.f., thus again showing the necessity of splitting our ordinary concept of impressed e.m.f. into these two aspects.

This fact, that there is no impressed driving e.m.f. at a bend in a crystal, I have verified by direct experiment, although protesting all the while that it was almost an insult to one's intelligence to make such an experiment. I made potentiometer measurements of the drop of potential between two points at opposite sides of a bend in a single crystal of bismuth (the crystal was cast with the bend in it), and verified that the potential drop is proportional to the current in the range of small currents and potential drops accessible to a high sensitivity galvanometer.

The physical explanation of the internal Peltier heat seems to demand the existence of some fine structure of which other phenomena give us little or no suggestion. There is no reason to think that this fine structure is confined to non-cubic crystals which have thermo-electric differences in different directions, but we must recognize its existence in cubic crystals as

well, that is, in all ordinary metals. In ordinary cubic metals this fine structure has the same properties in all directions, and therefore does not force itself on our attention when the direction of current flow changes. It seems to me that the recognition of this structure or mechanism must revolutionize our attempts at a theory of metallic conduction. It was my former opinion that theories of conduction need have little or no regard for thermo-electric phenomena, since there seemed no simple connection between the two classes of phenomena, but the discovery of the internal Peltier heat entirely alters the situation, and demands that the two phenomena be treated inseparably in any theory.

By the same argument as that used in the first part of this paper, we must recognize that the energy absorbed by the current as internal Peltier heat when the direction of flow changes must still be classified as thermal energy after it has been absorbed by the current. This much restricts any mechanistic explanation that we can offer of the phenomenon. For instance, we cannot say that when the electron turns the corner it moves against an equivalent microscopic potential difference.

There is a possibility of explanation in terms of the same "grooves" that I have imagined in connection with other phenomena. There are a number of indications that the electron in a solid metal can move only along certain grooves; in this case the existence of an internal Peltier heat would demand that the thermal energy of an electron in a groove would depend on the direction of the groove. This evidently means that we must give up equipartition, at least in detail. This remark applies to my own theory of metallic conduction, as well as to others. From the fact that the internal Peltier heat in bismuth is of the same order of magnitude as the total energy of a degree of freedom, we may infer that in spite of the failure of equipartition, the thermal energy of the electrons is of the same order of magnitude as that demanded by equipartition. The effect may well be some sort of quantum effect, and depend on the fact that the characteristic frequency of the electrons in the different grooves is different. A physical basis for this variation of frequency with direction is evidently afforded by the different lattice spacings in different directions.

It is obvious that there is a simple connection between the internal Peltier heat when the direction of current flow changes from the angle α_1 with the axis to the angle α_2, and the difference of ordinary Peltier heat when the current emerges from the crystal in different directions. If we denote internal Peltier heat by Π, then obviously

$$\Pi_{\alpha_1\alpha_2} = P_{\alpha_1 x} - P_{\alpha_2 x} = P_{\alpha_1\alpha_2},$$

where the subscript x denotes any isotropic metal into which the current flows at the interface.

We are now in a position to consider certain other effects in crystals. We must first recognize the possibility of a Volta difference of potential between faces of different orientations. We have already seen that the jumps of potential which are involved in this Volta difference are situated entirely

in the free faces of the crystal; there can be no jump at the interface in the metal. Of course in the case of ordinary metals there has long been difference of opinion as to the way in which the Volta difference should be divided between the two free surfaces and the interface. It is most interesting that we can here give definite proof that there can be no jump at the interface. It is tempting to extend this result to all metals, and to say that there can never be any Volta jump at an interface between two metals, but I can see no way of passing from the one case to the other. We may, however, draw the conclusion that the jump of potential at an interface between an isotropic metal and a crystal is independent of the orientation of the face of the crystal.

There is no experimental evidence of which I know bearing on the question of a crystalline Volta effect. It would not be easy to find it by experiments in vacuum, because of the extreme sensitiveness of the effect to slight variations in the surface conditions. There is one consideration which gives a certain plausibility to the expectation that the crystalline Volta effect may be zero. We have the photo-electric equation $\epsilon V_{AB}=h(\nu_{0A}-\nu_{0B})$ for the two metals A and B. This formula applies equally well to two different faces of the same crystal. Now it is not unreasonable to expect that the characteristic frequency ν_0 will be found to be independent of the orientation of the face, for the reason that it is known that in isotropic metals ν_0 is independent of the direction of polarization of the incident light. But until direct experimental proof is given, we must recognize the possible existence of this Volta effect. This effect means an intense field of force at the corners of a crystal. At temperatures high enough for the electron emission to be appreciable this means a different density of the electron atmosphere in equilibrium with the metal at different faces. This would lead us to expect also a different latent heat of evaporation at different faces. This difference of latent heats may, in fact, exist, whether or not there is a Volta difference.

The analysis of my former paper on the Volta and allied effects applies at once to many of the effects in crystals. In particular, I showed in that paper that there is a surface heat involved in charging a surface. In the crystal this surface heat is a function not only of the orientation of the surface, but also of the direction of motion of the charge in the crystal as it is brought up to the face. We must accordingly use a double subscript notation for this surface heat, one subscript to denote the orientation of the surface which receives the charge, and a second subscript to denote the direction of motion of the charge in the crystal. Thus $(P_s)_{\gamma\delta}$ means the heat absorbed when unit charge is added to a surface inclined at the angle δ with the principal axis of the crystal by being brought up to the surface along a direction inclined at the angle γ to the axis. It can now be shown at once, by carrying a charge around the two paths indicated in Fig. 6, that

$$(P_s)_{\alpha\gamma}-(P_s)_{\beta\gamma}=P_{\alpha\beta},$$

where $P_{\alpha\beta}$ is the ordinary Peltier heat at a crystalline interface, and is also, as we have shown, the internal Peltier heat when the direction of current flow inside the crystal changes from α to β.

We must now recognize that the latent heat of evaporation also depends on the orientation of the surface, and the direction in which the charge is brought up to the surface. Carry unit charge around the circuit shown in Fig. 7. The total heat absorbed in this circuit is zero, because it is described under equilibrium conditions at constant temperature. If the circuit is

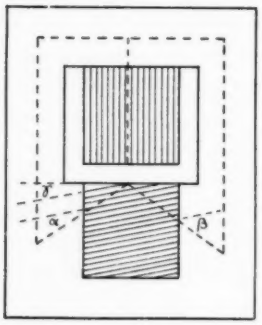


Fig. 6.

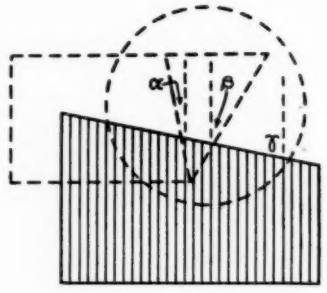


Fig. 7.

varied in any way that we please inside the region shown by the dotted circle, there is no change in the total heat, and therefore the heat absorbed in the dotted region is constant. First, carry charge across the surface at the angle β, and secondly, change the direction of motion, and carry across the surface at the angle α. On equating the heat absorbed in the two cases we obtain

$$(\eta_\rho)_{\beta\gamma}-(\eta_\rho)_{\alpha\gamma}=P_{\beta\alpha},$$

where η_ρ denotes the latent heat at *constant* surface charge. It is this heat which is usually given directly by experiment, charge being brought up to the surface as fast as it evaporates.

We have now to distinguish another latent heat, when the electrons are allowed to evaporate from the insulated metal, leaving behind a charge on the surface. It is this latent heat which is given by the usual thermodynamic analysis, and which enters Clapeyron's equation. This latent heat I have called η, without the subscript. There is a connection between the two latent heats and the surface heat, namely $P_s+\eta=\eta_\rho$. Now apply this to the face of the crystal, the surface being inclined at the angle γ, and the charge being carried through the surface, first at the angle α, and then at the angle β.

$$(P_s)_{\alpha\gamma}+\eta_{\alpha\gamma}=(\eta_\rho)_{\alpha\gamma}$$
$$(P_s)_{\beta\gamma}+\eta_{\beta\gamma}=(\eta_\rho)_{\beta\gamma}.$$

Subtracting these two equations, and using the relations found above for η_ρ and P_s, we obtain

$$\eta_{\alpha\gamma}=\eta_{\beta\gamma},$$

or the latent heat of evaporation at variable charge is independent of the direction in which the charge is brought to the surface within the metal.

This is as it should be, because the thermodynamic analysis employed in deducing Clapeyron's equation is concerned only with the initial and final states, and not with the details of the process.

There are many other interesting questions connected with the thermoelectric behavior of crystals, which cannot, however, be discussed here. One of the most important of these concerns the nature of the symmetry of the Peltier heat. This I regard as a question for experiment to decide. Experimental examination of this question has been made both by Linder and myself. The last paper of Linder[3] takes issue with some of my conclusions, and seems to call for some comment from me. I can only say that at present I am satisfied with neither the measurements of Linder or myself, and that I am undertaking a fresh experimental examination of the question, which will, I hope, lead to more satisfactory conclusions.

THE JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY, CAMBRIDGE, MASS.

[3] E. G. Linder, Phys. Rev. **29**, 554 (1927).

THE PHOTOELECTRIC AND THERMIONIC WORK FUNCTIONS OF OUTGASSED PLATINUM

By Lee A. DuBridge*

Abstract

In extending results previously reported the photoelectric and thermionic work functions for platinum were studied while the specimen was put through an extended outgassing process. With monochromatic light the final value of the photoelectric threshold was found to be 1962A (6.30 v.) The thermionic work function increases during outgassing, reaching a final value of 6.35 volts, within 1 percent. The two work functions are thus in agreement within the limits of error. The thermionic constant A of the Richardson T^2 law also increases as the work function increases, reaching a final value which is 200 times or more greater than Dushman's theoretical value of 60.2 amp/cm^2 deg^2.

IN TWO previous articles [1,2] the writer has presented the results of a study of the photoelectric properties of platinum when the surface of the metal is thoroughly cleaned of occluded gases. With light filters to cut out successively the shorter lines in the spectrum of the quartz mercury arc, it was found that the photoelectric threshold for platinum shifted steadily toward the shorter wave-lengths during outgassing, and after prolonged treatment in the highest attainable vacuum reached a final value somewhere between the mercury lines 1943 and 1973A. In extending these results it seemed worth while to determine this limit still more accurately using monochromatic light, and to compare the value of the photoelectric work function so found with the value of the thermionic work function for the same specimen.

Previous attempts to establish the identity of these two quantities for the various metals have succeeded only in the case of tungsten, for which Warner[3] has recently found that after careful outgassing the two work functions are equal within the limits of experimental error. In the case of platinum recent attempts[4] to make a direct comparison of the two "constants" have led to inconclusive results because of the very great difficulties in eliminating the effects of gases. Suhrmann[5] has reported a check between the two, giving 4.6 volts as their common value. However this value for the photoelectric work function (corresponding to a threshold of 2675A) is clearly too low for the outgassed metal in the light of the recent results of Tucker,[6] Woodruff[7] and the author.[2]

* National Research Fellow.

[1] DuBridge, Nat. Acad. Sci. Proc. **12**, 162 (1926).

[2] DuBridge, Phys. Rev. **29**, 451 (1927).

[3] Warner, Nat. Acad. Sci. Proc. **13**, 56 (1927).

[4] Harrison, Phys. Soc. Lon. Proc. **38**, 214 (1926).

[5] Suhrmann, Zeit. f. Physik. **13**, 17 (1923).

[6] Tucker, Phys. Rev. **22**, 574 (1923).

[7] Woodruff, Phys. Rev. **26**, 655 (1925).

A large number of experimental values for the thermionic work function alone for platinum have been reported by various observers, but it is notable that the excellent agreement between results found for metals such as tungsten and molybdenum is completely lacking in the case of platinum. The reported values for this metal are well scattered in the range from 4.0 to 6.6 volts,[8] the range between 5.0 and 5.5 volts being perhaps slightly

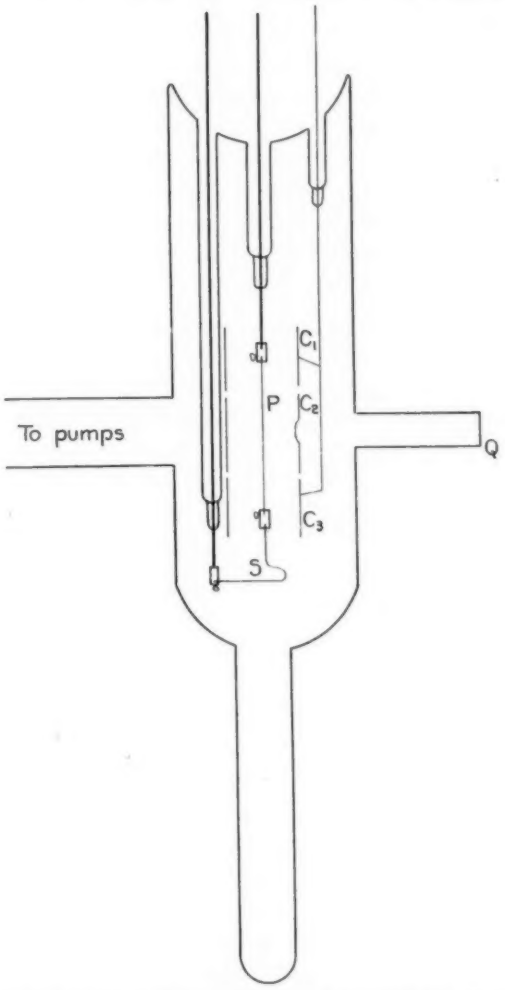


Fig. 1. Tube for study of photoelectric and thermionic properties of Pt.

favored. It has been shown many times that very slight amounts of gas in the surface could produce enormous changes in the thermionic emission, and H. A. Wilson[9] was able to reduce the work function for a platinum specimen to as low as 2.2 volts by heating in an atmosphere of hydrogen. A systematic study of the behavior of the thermionic work function *during*

[8] See Richardson "Emission of Electricity from Hot Bodies" 2nd ed. p. 81.
[9] Wilson, Phil Trans. **208A**, 251 (1908).

the outgassing process seemed therefore desirable in order to determine the limit which this quantity would approach as the thoroughly outgassed state is reached.

Apparatus. The tube used was of the form shown in Fig. 1. The specimen to be tested was a strip of platinum foil, P, 5 cm long, 2 mm wide and about 0.01 mm thick, suspended along the axis of the collecting cylinder C and the coaxial guard ring cylinders C_1 and C_2. The latter cylinders served to collect spurious photoelectric and thermionic currents from the clamps supporting the strip and from the cool ends of the strip itself. The three cylinders were rigidly supported from a pair of Pyrex rods not shown in the diagram. The strip could be heated by an electric current conducted in through heavy tungsten leads. It was kept taut during heating by the weight of the lower clamp, which was a small nickel block attached to the tungsten lead through the flexible copper strip S. The temperature of the platinum was determined with an optical pyrometer focussed through the window Q, correction being made for the transmission of the window and the emissivity of platinum. The temperature scale of Mendenhall[10] was used, though this is in substantial agreement with the more recent one of Worthing[11] in the range of temperature used for the thermionic measurements. The window Q which was of quartz, sealed directly onto a graded quartz to Pyrex seal, served also to admit light from a quartz mercury arc, resolved by a Fuess quartz monochromatic illuminator. The currents to the collecting cylinder were measured by means of a Compton electrometer whose sensitivity at the scale distance used (3 meters) could be brought to 30,000 mm/volt. A series of high resistance shunts was used for measuring the thermionic currents, but the very minute photo-currents were measured by the "rate of charge" method.

The pumps, vacuum conditions and outgassing methods were similar to those used in the previous experiments at the University of Wisconsin. The entire glass system was of Pyrex and all glass on the high vacuum side was thoroughly baked out at temperatures up to 550°C before any measurements were begun. All waxed and greased joints were eliminated from the high vacuum side of the pumps, an important point since much of the previous difficulty in obtaining consistent and reproducible results for platinum can undoubtedly be traced to the presence of organic vapors due to such joints.[12] In one test run made by the writer it was found that sealing off a side tube which contained a wax joint caused an immediate rise in the thermionic work function of the specimen under test from 5.2 to 6.0 volts.

The photoelectric threshold. In order to determine the photoelectric threshold by the usual method the relative intensities of the lines of the mercury spectrum must be known. These were measured for the lines longer than 2200A with a vacuum thermopile and the results checked with those obtained by Kazda[13] for an arc operating under identical conditions.

[10] Mendenhall, Astrophys. J. **33,** 91 (1911).
[11] Worthing, Phys. Rev. **28,** 174 (1926).
[12] This may be the cause of Suhrmann's low value for the work function for *Pt.*
[13] Kazda, Phys. Rev. **26,** 643 (1925).

However the three shortest lines in the spectrum, λ1849, 1943 and 1973A are far too weak to produce a measurable effect on the thermopile, and the previous work had shown that these were just the lines required to determine the threshold for the thoroughly outgassed platinum. Their relative intensities were therefore estimated by the following method. Using a fresh platinum specimen whose threshold was near 2540A the measured photoelectric currents were plotted as a function of the wave-length of the incident light, as read from the drum of the monochromatic illuminator. (Since the drum was originally calibrated only to 2000A it was necessary to shift the prism table and recalibrate the drum to make all lines down to λ1850 available.) The various lines in the mercury spectrum below 2540A then appeared as peaks on this photoelectric curve. Then using the lines for which the relative intensities had been directly measured, the photocurrent per unit intensity was plotted as a function of wave-length. This of course gave a regular curve which could be extrapolated to the shorter wavelengths and the effective intensities of the shorter lines could be deduced, since the photo-currents produced by them had been measured. In making the extrapolation use was made of the following equation for the efficiency of photoelectric emission as a function of frequency recently derived by Uspensky[14] and shown to hold for platinum over a wide range of frequencies.

$$i = (\text{const.}\ /h\nu)\left[(\nu/\nu_0)^{1/2} + (\nu_0/\nu)^{1/2} - 2\right].$$

In this equation i represents the photo-current excited by unit intensity of incident light, ν is the frequency of the incident light and ν_0 the threshold frequency. The equation was found to fit the experimental points quite closely and the intensities of the three shortest lines in the spectrum were determined to make their points fall on the curve.

The intensity of λ1849 relative to λ2536 as deduced by this method is approximately 1.8×10^{-5}, and the relative intensities of the three lines, 1849, 1943, and 1973A are in the ratio 1.8:10:13. The computed intensities of these lines *relative to each other* are not much affected by probable errors in extrapolation. All the intensities determined in this manner gave completely consistent results throughout the experiments.

The behavior of the photoelectric threshold during the outgassing of a typical specimen is shown in Fig. 2 in which the photo-current per unit intensity of incident light is plotted as a function of wave-length of the light. Curves I, II, III, and IV represent runs taken at successive stages in the outgassing process. Curve I was taken with a fresh specimen after the initial baking of the tube, and shows a threshold at 2540A. This initial value varied considerably for different specimens. The state represented by curve IV was reached only after 100 hours or more of heating at 1200°–1500°C in the highest attainable vacuum. Continued heating and baking then produced no further change in the curve. When this steady state has been reached—and not before—the photo-currents and the threshold value are

[14] Uspensky, Zeits. f. Physik. **40**, 456 (1926).

perfectly stable and reproducible as long as the vacuum remains unimpaired. Allowing the liquid air around the charcoal tube to run low however causes an immediate rise in the photo-currents and a shift of the threshold toward longer wave-lengths. It is believed that curve IV represents the state of affairs for the most completely outgassed state of the platinum which it is possible to reach by the present method of heat treatment. It will be seen that the threshold for this state is approximately 1962A. This value is in agreement with the previous work with filters and was repeated quite closely for other specimens put through slightly different forms of treatment. It was also repeated for specimens which had been put through a complete series of thermionic measurements as described in the next section. *The*

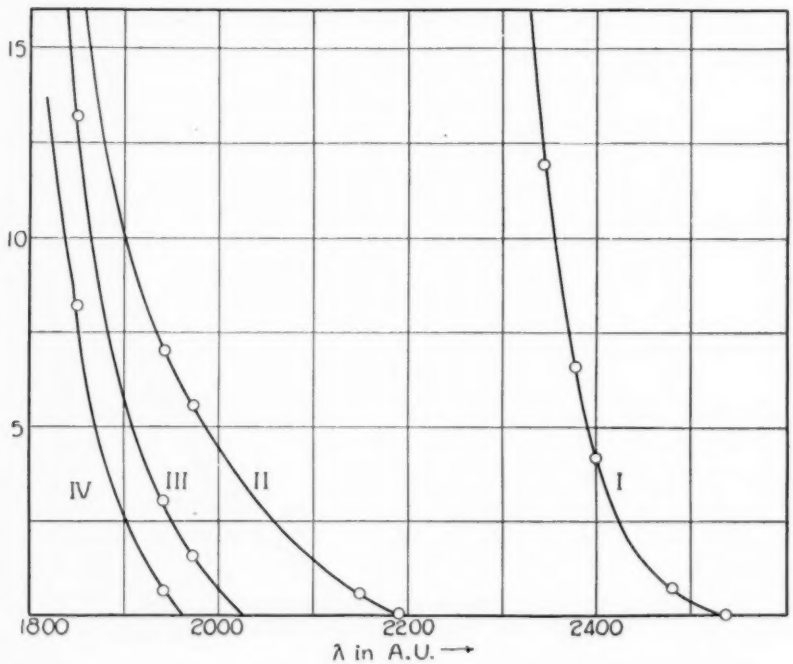


Fig. 2. Photoelectric curves for Pt during successive stages of outgassing.

photoelectric work function for outgassed platinum is therefore 6.30 volts, with a probable error of not more than 0.5 percent. This value may of course be slightly further reduced when better vacuum conditions and outgassing methods become available.

The thermionic work function. A study of the behavior of the thermionic work function during outgassing showed at once that the thermionic currents were even more sensitive to slight traces of gas than were the photo-currents. Thus with the tubes connected to the pumps it was found nearly impossible to reach a state where consistent reproducible values of the work function could be obtained. The *average* values obtained showed a consistent increase during outgassing from about 4.6 volts for a fresh specimen after a thorough

initial baking to something over 6.0 volts after prolonged heating. The deviations from the mean value were however sometimes as great as 50 percent for a fresh specimen, though they could be reduced to 5 percent after long treatment.

After burning out several strips in unsuccessful attempts to bring them to a more steady state by more intense heating, the tube was finally arranged so that it could be sealed from the pumps and a small amount of magnesium vaporized in the lower part to act as a "getter." After a few hours of heating under these conditions (after 100 hours or more of heating before sealing off) and with the charcoal tube immersed in liquid air, the erratic behavior soon ceased and consistent values of the emission and the work function could be

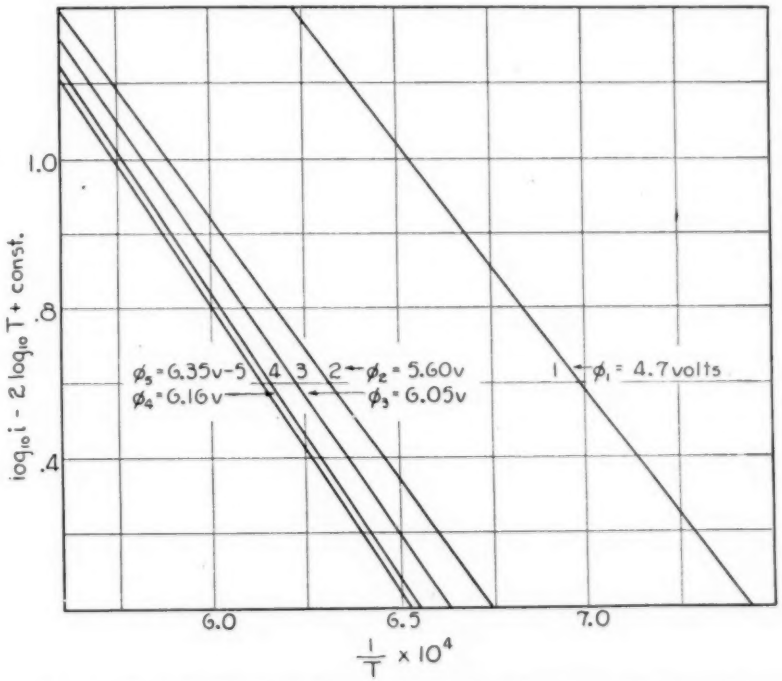


Fig. 3. Thermionic curves for Pt during successive stages of outgassing.

obtained. The behavior of a typical specimen during outgassing is shown in Fig. 3 in which the usual "Richardson straight lines" are plotted for successive stages in the outgassing process. The slopes of these lines are proportional to the work function b of Richardson's T^2 law. Curve 5 is the final one obtained after sealing off the tube. The photoelectric curve for this same specimen, after sealing off, coincided with curve IV of Fig. 2. It will be seen that the final value of the thermionic work function, 6.35 volts, is in remarkably good agreement with the photoelectric value. This final value varied somewhat from specimen to specimen but never differed by more than 0.1 volt from the above value. The error due to the uncertainty in the temperature scale may be as large as this. *The agreement between the photo-*

electric and thermionic work functions for outgassed platinum is thus established, within the limits of error.

Two points in connection with the thermionic emission from partially outgassed specimens may be of interest. In the first place the thermionic straight lines for such specimens sometimes showed abnormally large slopes, corresponding to work functions as high as 7.0 volts. It was found that this was due to a progressive change in the sensitivity of the specimen during the time the run was in progress, and was not a real characteristic of the platinum. This is mentioned merely to indicate that values of ϕ_0 higher than 6.35 volts which have been reported by other observers[7,15] are not necessarily indications that a more completely outgassed state of the platinum had been reached than was attained in the present work.

In the second place it was found that the thermionic emission from fresh platinum specimen was in many ways analogous in its behavior to that from thoriated tungsten filaments. This suggests that perhaps the same sort of diffusion and evaporation process is taking place in the two cases, and it is natural to assume that the hydrogen absorbed in the platinum plays the role of the thoria in the tungsten. Many peculiar effects in the behavior of both photoelectric and thermionic currents from partially outgassed specimens can be interpreted on the basis of this analogy.

The thermionic constant A. As a result of the simple geometrical arrangement of the emitting surface and collecting cylinder in the present experiments it was possible to compute the absolute value of the thermionic current per unit area of emitting surface with reasonable accuracy and thus to determine the constant A in the Richardson T^2 law. Richardson and Dushman[17] have suggested that A should be a universal constant for clean metals having the value 60.2 amp/cm^2 deg^2. Dushman[18] has confirmed this value (roughly at least, since very accurate determinations of A are nearly impossible) for the case of tungsten, tantalum and molybdenum. On computing the value of A from carefully taken emission data on several outgassed platinum specimens in the present work however, values 200 times or more as great as the theoretical value were obtained. Fresh specimens on the other hand gave values of A considerably too low. In fact there is a very definite increase in A accompanying the increase in b or ϕ_0 which takes place during outgassing. This increase in A becomes more rapid as outgassing proceeds and on plotting it was found that log A is roughly proportional to b. In one particular case as ϕ_0 for a specimen increased from 4.7 to 6.4 volts during outgassing the corresponding values of A increased from 11.5 to 14,000. Moreover the values of A and b obtained by other observers for platinum show this same behavior, a fact which has been mentioned by Richardson[16] and by H. A. Wilson.[9] This is clearly shown in the following

[15] Langmuir, Phys. Rev. **2**, 450 (1913).
[16] Richardson, "Emission of Elect. etc" p. 137.
[17] Dushman, Phys. Rev. **21**, 623 (1923).
[18] Dushman, Phys. Rev. **25**, 338 (1925).

table in which are collected values of A and b and ϕ_0 obtained by various observers along with some of the values obtained in the present work. As would be expected the individual values of A are somewhat scattered but the general trend is unmistakable.

The values of A found by the author for thoroughly outgassed specimens when conditions were at their best ran consistently between 10,000 and 20,000. The order of magnitude of A for cleaned Pt is thus definitely greater than that required by Dushman's theory.

TABLE I

Concurrent variations of thermionic constants.

Author	b(deg K)	ϕ_0(volts)	A(amp/cm^2 deg^2)
Wilson[9]	25,600	2.18	10.7×10^{-4}
Richardson[8]	47,500	4.10	39.8
Du Bridge	54,500	4.69	11.5
Deininger[19]	58,500	5.02	16.2
Wilson[9]	63,000	5.45	366.
DuBridge	65,000	5.60	235.
Richardson[8]	65,500	5.65	265.
Wilson[9]	70,000	6.00	620.
DuBridge	72,000	6.20	6450.
"	73,000	6.30	8130.
"	74,200	6.40	14000.
Langmuir[15]	77,000	6.62	$107.\times10^6$

The relation between A and b shown in Table I has also been found for other metals. Thus Kingdon[20] found that if a clean tungsten surface is coated with oxygen the work function of the surface increases from 4.5 to 9.2 volts and at the same time the value of A increases from 60 to 5×10^{11}. Coating a tungsten surface with thoria reduced the value of ϕ_0 to 2.68 volts and A to approximately 7, while coating with caesium reduced ϕ_0 to 0.715 volt and A to 10^{-3} amp/cm^2 deg^2. It thus appears that this direct connection between A and b may be quite general, applying to all surfaces, and that Dushman's value of A is obtained experimentally only for those surfaces for which ϕ_0 happens to have the value characteristic of clean tungsten or molybdenum, namely 4.5 volts. Further investigation of this point seems desirable.

The author is greatly indebted to Professor Millikan and the staff of the Norman Bridge Laboratory for the facilities placed at his disposal.

CALIFORNIA INSTITUTE OF TECHNOLOGY,
October 26, 1927.

[19] Deininger, Ann. d. Physik. **25,** 285 (1908).
[20] Kingdon, Phys. Rev. **24,** 510 (1924).

THE CONTACT POTENTIAL BETWEEN THE SOLID AND LIQUID PHASES OF BISMUTH

By Philip H. Dowling

Abstract

Contact potential between the solid and liquid phases of bismuth.—In order to obtain as gas-free metal as possible, the bismuth was distilled into the highly exhausted apparatus. The contact potential was measured, by the standard Kelvin method, against a copper plate whose absolute potential was maintained constant by protecting it from the temperature changes incident to melting and solidifying the bismuth. The results were remarkably free from disturbing factors which arise from residual gas effects. Solid bismuth was found to be of the order of -0.020 volts with respect to the molten metal. Small variations from this value were caused, presumably, by the chance crystalline state of the solid surface.

Relation between thermo-electric power and temperature change at contact potential.—The equation $dV/dt = dE/dt$, which expresses the equality of the thermo-electric power to the temperature rate of change of contact potential, has so far failed of experimental verification. The present experiment, though not adapted to a real test of the equation, yielded evidence that the discrepancy can be greatly reduced by improvement of experimental conditions.

The effect of surface charges on melting conditions.—From the results on the contact potential between the two phases of bismuth, it can be shown thermodynamically, following Bridgman's treatment of the matter, that, when one coulomb per cm² is added to the surface of bismuth at constant volume, pressure, and capacity the melting point of the metal increases by $(1/v)\times 0.02$°C where v is the volume per unit area of the solid bismuth at its melting point.

IN A previous paper,[1] the author reported some work on the contact potential between the solid and liquid phases of various low melting-point metals such as tin and lead-tin alloys. At that time it could not definitely be established that a metal, in passing through its melting point, changed its contact potential relative to another metal whose condition had remained fixed. This negative result was ascribed to the masking of any small, real effect by a residual gas effect.

To eliminate this gas effect, it was decided actually to distill the metal under investigation into the highly exhausted apparatus. Bismuth presented itself as a most satisfactory metal for the experiment. Its melting point (271°C) is not too high to render impracticable the use of the direct Kelvin method for the measurement of the contact potential. At this temperature its vapor pressure is negligibly small (10^{-10} mm of mercury), so that contamination of the measuring plate is not to be feared, although at 900°C, it is high enough for reasonably rapid distillation. Furthermore, one has an instinctive feeling that if there is an effect to be shown, bismuth will show it. As will appear later, the one bad feature in using bismuth for the author's purpose is its expansion as it solidifies.

[1] Dowling, Phys. Rev. **25**, 812 (1925).

Since it had to withstand, evacuated, a temperature of 900°C; the still, *S* (see figure), was constructed of quartz. At first this was sealed to the main tube of Pyrex glass by a graded quartz-to-Pyrex seal and considerable time was wasted in the construction of such seals by the author and in trying out seals purchased on the market. In either case, no matter how rugged a seal appeared to be, the present requirements were too severe for it and it would eventually crack. The problem of sealing the quartz still to the tube was finally solved by the use of a ground joint, *B*, surrounded by a glass cup. This cup was filled with molten tin which rendered the joint vacuum tight, allowed the joint to be baked out, and made dismantling of the apparatus relatively easy. The tin was kept melted throughout the entire course of the experiment by a small electric furnace. Since the vapor pressure of tin at its melting point is but 10^{-20} mm of mercury, contamination of the bismuth from this source was negligible. The still was heated by an electric furnace and had, also, to be kept hot (above 271°C) throughout the entire experiment; for if the bismuth remaining in the still had solidified, it would have cracked the quartz. The construction of the still gave an excellent regurgitating action during distillation and the results gave every indication that the bismuth had been very well outgassed.

The preparation of the bismuth surface was as follows. The still was filled with small pieces of bismuth which was the residue from a previous distillation. After the all-glass tube had been sealed, it was exhausted by a conventional pumping system and baked to a temperature of 400°C by means of an electric furnace which completely surrounded it, including the still furnace. A higher baking temperature was not thought necessary from the point of view of the subsequent temperatures to which the tube was to be exposed and would have endangered the working of the various mechanical parts of the apparatus. As soon as the McLeod gauge showed a "sticking vacuum," the carriage *C* was moved with a magnet until the little cup *D* was under the discharge of the still. The latter was then heated to 900°C while the whole tube was kept just above 271°C. In this manner bismuth was distilled as a liquid into the small cup and the initial, poorly outgassed metal was removed, together with any dust which might have accumulated in the still. When *D* was filled, *C* was moved until the glass tube *F* brought the still discharge into communication with the crucible *L* in which the metal was to be held during measurement. Possibly six hours were required to fill the latter. After cooling the main tube but keeping both the residual bismuth in the still and that in the measuring crucible above 271°C and the tin joint above 230°C, the McLeod gauge showed a "sticking vacuum" of between four and five cms.* After the distillation, *C* was moved out of the way of the measuring apparatus.

This latter consisted of a nickel plate, *H*, connected to the electrometer through a fine nickel spring and insulated from its housing *I* and lifting armature *A* by quartz *Q*. Any change in capacity between *I* and *H*, as the

* Two mm at the top of the gage capillary represented a pressure of 0.00001 mm of mercury.

latter was raised in the process of taking a reading, was minimized by the shield J connected to H. Such a change would have affected the electrometer and falsified the readings. J also insured a minimum effect on the readings of the edges of the crucible holding the bismuth. I, being earthed, served as an electrostatic shield from stray charges on the walls of the surrounding glass tube. An earthed wire gauze around the outside of the glass tube provided further shielding. This mounting for the movable plate was very compact, fitting inside a two-inch tube, and gave very satisfactory results. The whole affair could be moved along the tube, sliding on the same tracks P as did the delivery tube F, so as to be over either the bismuth or a standar-

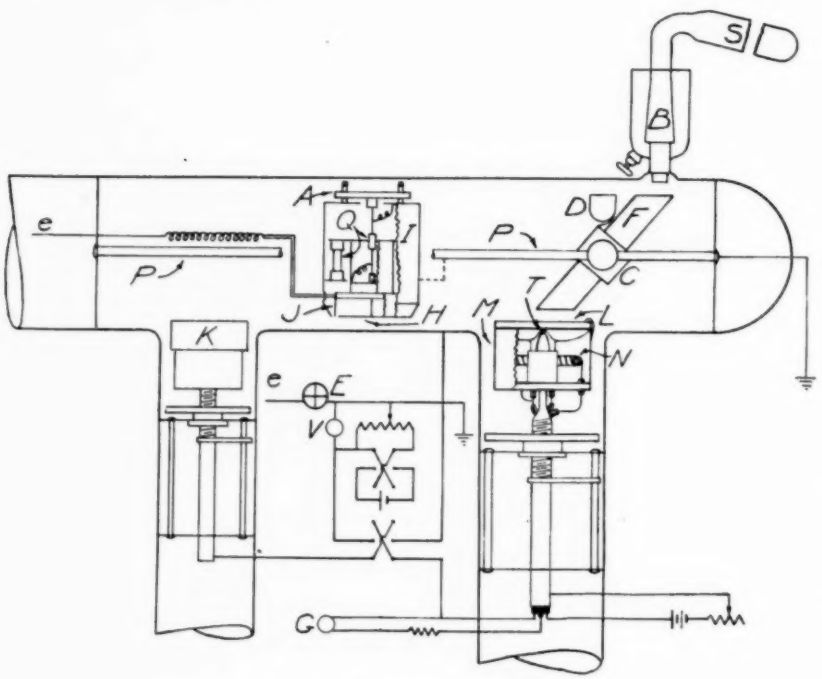


Fig. 1. Diagram of apparatus.

dizing plate. Details of the guides for the measuring apparatus have been omitted in the figure for the sake of clarity.

Since the contact potential between two metals is given to a first approximation by the difference between the work functions of the two surfaces, a measured change in the contact potential cannot be traced to either surface unless some means is at hand for standardizing one or the other. In the present work, the temperature of the nickel measuring plate varied with that of the bismuth and since it could not be thoroughly outgassed without increasing the complexity of an already too complicated apparatus, its work function could not be expected to remain constant. A solid piece of copper, K, was used as a standard plate whose large thermal capacity and radiating surface were relied upon to keep its temperature sensibly constant

even though small amounts of heat were conveyed to it by the nickel plate. K was mounted on a screw so that by means of a magnet outside the tube its height could be adjusted to correspond with that of the measuring plate. No special care beyond careful mechanical cleaning was taken in the preparation of either the copper or nickel surface. The former was found to be indispensable and the nickel plate was checked against it before and after every reading on the bismuth surface.

Considerable difficulty was encountered in the choice of a material for the measuring crucible L. Although no apparent trouble had been experienced in previous work with graphite crucibles, it was found impossible, in the present instance, to prevent small particles of graphite from shearing off and floating on the surface of the molten bismuth. Carbon, though harder, could not be rid of carbon dust left by the tool in its forming and moreover was much more difficult to outgas than the graphite. Metals were shunned for fear of contamination of the bismuth by alloying. On the supposition that its coat of oxide might protect it, aluminum was tried but under high vacuum conditions it alloyed in spots with the bismuth. Although previous experience had shown that one must be wary of tribo-electric effects[1] in using glass for such a purpose, the crucible was finally made of Pyrex glass. The tribo-electric effects were avoided by the simple expedient of never cooling the bismuth more than a few degrees below its melting point. The crucible was made an inch and a quarter in diameter and an eighth of an inch deep with a small reentrant tip in the bottom to accommodate a thermocouple. Electric contact was established with the bismuth by a fine tungsten wire bent over the crucible edge. Since the nickel measuring plate was but seven-eighths of an inch in diameter, the crucible edge was fairly well removed from it and moreover the molten bismuth surface was sensibly flat over the area of the plate in spite of surface tension effects. Curvature of the bismuth surface was to be avoided since it reduced the sensitivity of the measuring apparatus. The crucible was mounted as the cover to a cylindrical nickel box, M, which contained a small nichrome helix wound on a quartz ring, N. A current of about an ampere through the helix sufficed to keep the bismuth in the neighborhood of the melting point. Care was taken, of course, to heat the nichrome during the outgassing process well above its final operating temperature. The iron-nickel thermocouple T, though hardly fit for precise measurements, by reason of the necessary unprotected junctions with foreign metals, was found fairly reliable and was used satisfactorily to pick out the melting point by the flattening of the cooling curve. In order to adjust its height to that of the measuring plate, the entire crucible system was mounted on a screw similar to the mounting of the standard plate.

In the author's previous work, it was possible to take readings right through the melting point. The bismuth, at least in the apparatus used, did not allow this because of its large expansion on solidification. The consequent change in level of the surface, made necessary a readjustment, just at the melting point, of the screw upon which the measuring crucible was mounted. This condition was aggravated by the propensity of the metal

to commence solidification near the edges of the crucible and then, just before the last surface metal in the centre of the crucible hardened, to push up a small peak, as much as an eighth of an inch high and an eighth in diameter. Not only did this reduce enormously the sensitivity of the Kelvin method for measuring the contact potential of the solid surface but it was found that any scum-like impurity (which surface tension effects would ordinarily keep down under the curved edge between the molten metal and the glass) would follow the line of solidification and finally locate at the very top of this peak. Nor was the author ever able; even with the utmost care in cleaning the parts to come in contact with the bismuth, in predistilling the metal, or in discarding the first droplets of the metal as they distilled over; to get a surface entirely free from a small trace of a brownish scum which coagulated into a few minute spots and fortunately ordinarily remained under the curved edge of the molten metal. The origin of this scum remained a mystery. It could not be dissipated by making the melted bismuth the cathode of an electric discharge in hydrogen. Finally all attempts to get rid of it were abandoned and a policy of strict scrutiny of the surface adopted. As stated, it caused little trouble with measurements on the molten state and it was found possible to *occasionally* induce the metal to start solidification in the centre of the metal surface, leaving the undesirable peak at the edge of the crucible, safely out of range of the measuring apparatus. In such cases, it was indeed a beautiful sight to watch the growth of crystals in the surface. A tiny crystal might start in the centre, its presence betrayed only by the little surface tension ridge between it and the molten metal, and grow undistorted until its points reached the edges of the metal, when the remaining molten molecules would be forced to break the precedent set by their solid neighbors. In other cases, practically the whole surface might be covered with small crystalline facets. Great care was taken in watching the surface during solidification to see that no floating scum contaminated it.

During the four days of observations on the surface, only two complete runs; that is—comparisons between the contact potential, with respect to the copper plate, of the solid and liquid metal; were considered unimpeachable. By unimpeachable is meant, not that the measurements checked, but that the solid metal had a clean, flat, crystalline surface with no peaks beneath the measuring plate. Of these two solid surfaces, one was almost entirely a single triangular crystal, the edges near the crucible being filled in with a varied assortment of small crystals. It showed a contact potential with respect to the melted metal of -0.025 volts. The other was a maze of tiny facets and had a contact potential with respect to the liquid metal of -0.015 volts. These measurements had an accuracy such that 0.040, say, could be distinguished from 0.045 volts with certainty. That the results on these two surfaces do not check exactly may be ascribed to one of three possible reasons—difference in crystal structure, contamination in the form of scum, or residual gas effects. Contamination, the author feels certain, is ruled out.

As for residual gas effects, the author was very well pleased with the constancy of conditions in the tube. Throughout all the many measurements made on the molten surface, its contact potential with respect to the copper plate remained constant at +0.370 volts. In view of the notorious fickleness of contact potential measurements, this seemed quite remarkable. Further, the contact potential of either the solid or melted surface was insensible to temperature changes. The temperature of the solid surface was lowered 70°C below the melting point with no effect on its contact potential. It might have continued constant below this but the author was afraid of running into tribo-electric effects because of the glass crucible. The molten metal was carried 23°C above the melting point without changing its contact potential, above this, the nickel plate began to change so rapidly that it could not be checked precisely against the copper standard.

Since a difference of 0.005 volts could be detected in the present experiment; we can say, from the results stated in the previous paragraph, that, in the neighborhood of 270°C, the temperature rate of change of the contact potential between bismuth and copper, when the temperature of the bismuth only is varied, is less than 0.00007 volts/°C; *i.e.*—0.005/70. Although this process is not strictly that denoted by dV/dt, it is interesting to note that the figure 0.00007 is of the same order of magnitude as the thermoelectric power of a bismuth-copper couple.[2] This seems fairly strong evidence that the existing discrepancy of 50 fold[3] in the experimental verification of the equation $dV/dt = dE/dt$ may be greatly reduced. Here dV/dt is the temperature rate of change of contact potential and dE/dt the thermoelectric power between the same two metals.

The results on the change in the contact potential at the melting point are applicable to the hypothetical effect of surface charges on surface melting conditions. The relations between such effects and contact potential were discussed by Bridgman.[4] A slight modification of his treatment yields an equation from which may be calculated the magnitude of the change in the surface melting point, under constant pressure, volume, and capacity conditions, when unit density of charge is added to the surface. Setting up a condenser of which our bismuth is one plate, we may choose as independent variables; c, the capacity per unit area of the condenser; ρ, the density of charge on the bismuth surface; v, the volume per unit area of the bismuth; π, the hydrostatic pressure; and as dependent variables, V, the contact potential of the bismuth relative to the other condenser plate; u, the internal energy of the system per unit area; dW, the work per unit area done by the system in any infinitesimal change; dQ, the heat absorbed per unit area by the system in any infinitesimal change; t, the absolute temperature. It can then be shown thermodynamically that

[2] Existing thermo-electric data on bismuth seems to be rather sketchy. dE/dt for a bismuth-copper couple as calculated from Caswell's work (Phys. Rev. **33**, 381, 1911), is 0.00006 volts per °C at 18°C.

[3] K. T. Compton, Phys. Rev. **7**, 209 (1916) and **9**, 78 (1917).

[4] Bridgman, Phys. Rev. **14**, 306 (1919).

$$\partial V/\partial v=(1/t)\left[(V+\partial u/\partial \rho-\rho/c)\partial t/\partial v-(\partial Q/\partial v)\partial t/\partial \rho\right].$$

At the melting point, $\partial t/\partial v$ is zero, so for this temperature the equation reduces to

$$t\partial V/\partial v=-(\partial Q/\partial v)\partial t/\partial \rho.$$

Here the partial derivatives imply the constancy of the remaining independent variables. The equation may be rewritten

$$\partial t/\partial \rho=-t(V_L-Vs)/Lvd\ ;$$

where V_L-V_S is the change in the contact potential on solidifying the bismuth (+0.02 volts); L the latent heat of fusion of bismuth (−12.64 cal/gr.); d the density of solid bismuth at its melting point (9.8 gr/cm³); t the melting point of bismuth (544°K); v the volume per unit area of solid bismuth at its melting point (a constant depending upon the size and shape of the bismuth condenser plate). Substitution of these values gives,

$$\partial t/\partial \rho=(1/\mathrm{v})\times 0.02°\mathrm{C/coulomb\ per\ cm^2}.$$

The smallness of the effect is evident both from the smallness of the figure itself and from the magnitude of the coulomb. Since V is independent of v, we can say that the effect should be larger the larger the ratio of surface area to volume of the solid bismuth condenser plate at its melting point.

YALE UNIVERSITY,
June, 1927.

RESISTANCE CHANGE OF SINGLE CRYSTALS OF BISMUTH IN A LONGITUDINAL MAGNETIC FIELD

By G. W. Schneider

Abstract

Resistance change of single crystal Bi as a function of magnetic field intensity.—Bismuth crystals of various orientations (angle between vertical crystallographic axis and length of specimen) show an increase in resistance in a magnetic field parallel to the specimen length. The fractional change in resistance $\Delta r/r$ is shown to be proportional to a power, slightly less than two, of the field intensity. In a maximum field of about 3500 gauss and at room temperature the increases in resistance range from 2 to 9 percent.

Resistance change of single crystal Bi as a function of orientation.—For a constant magnetic field (3480 gauss), the change in resistance when plotted against crystal orientation, shows maxima at orientations of 63° and 80°, and minima at 0°, 73°, and 90°. This effect is substantiated by observations on specimens whose orientations have been changed by grinding or splitting, since these show the same type of variation with orientation as do the separate crystals. To determine whether the effect is due to a lack of rotational symmetry about the vertical axis some experiments are described in which the position of the vertical axis was kept fixed and the position of a minor (digonal) axis varied slightly. No observable change was found.

Specific resistance.—The specific resistance, as a function of crystal orientation obeys the Voigt-Thomson symmetry relation. Comparison with recent results by Bridgman show a considerable difference, the explanation of which has presumably been given by Bridgman.

Introduction

OBSERVATIONS on the change in resistance of bismuth caused by a magnetic field have been made by many experimenters.[1] The effect in specimens composed of single crystals of bismuth has been measured by van Everdingen,[2] Lownds[3] and Borelius and Lindh.[4] In all these cases the crystal specimens were rods or plates sawed or cut from a large crystal in such a fashion as to have the desired orientation. No systematic investigation seems to have been made of the resistance change as a function of the orientation of the crystallographic axes with respect to the longest dimension of the specimen (for a rod or wire). The work reported here was undertaken with the purpose of making such a systematic study. It is confined, however, to the longitudinal effect, that is, to a study of the resistance change caused by a magnetic field which is in the direction of the length of the wire. The magnetic field and current in the specimen are thus parallel.

[1] See Campbell: Galvanomagnetic and Thermomagnetic Effects (1923) for bibliography.
[2] Van Everdingen, Phys. Zeits. **2**, 585 (1900–01).
[3] Lownds, Phil. Mag. (6) **5**, 141 (1903) and Ann. d. Physik. (4) **9**, 677 (1902).
[4] Borelius and Lindh, Ann. d. Physik (4) **53**, 97 (1917–18).

The bismuth crystal[5] appears to belong to the trigonal system, ditrigonal-scalenohedral class, dihexagonal alternating type. It may be referred to rhombohedral axes, equal in length and mutually inclined at an angle of 87° 34′. The (111) plane is then the plane of easiest cleavage, is perpendicular to the trigonal, or vertical axis, and contains three digonal axes. A second cleavage which is apparently along a $(11\bar{1})$ plane[6] also exists. Rhombohedral cleavages were not observed in the specimens described below. In what follows the angle between the vertical axis and the length of the specimen is defined as the orientation. Positions of the digonal axes are not specified, since it was assumed at first that bismuth crystals have rotational symmetry about the vertical axis. For this and similar types of crystal, this assumption is certainly justified for many other properties, as has been shown by, or may be inferred from, the work of Bridgman,[7] Grüneisen and Goens,[8] Linder,[9] Boydston,[10] etc. This point will be discussed further below.

The crystals were prepared and orientations measured as described by Linder[9] and Boydston.[10] The bismuth used was the same as that used by Boydston.

Description of Apparatus

The magnetic field was produced by means of a solenoid made up of 155 turns of 0.8 cm copper tubing wound in five layers over a hollow cylindrical brass core. This core was 25.4 cm long, and 3.8 cm outside diameter. The constant for the solenoid was 7.33 gauss per ampere at the center and 7.15 gauss per ampere 5 cm either side of the central position, the average being 7.24. The solenoid was cooled by circulating water through the copper tubing. The water inlet was at the middle of the winding while the two ends of the solenoid served as outlets. Thus the water flowed from the center of the winding to both ends, producing efficient cooling. A General Electric 5 KW 10 volt generator was used to obtain the magnetizing current. This current was controlled by variation of the generator field by means of rheostats and a lamp bank.

The crystal was placed in a longitudinal groove in a wooden cylinder which fitted in the brass core of the solenoid. Two brass lugs were soldered to the ends of the crystal. They were allowed sliding room in case of any motion of crystal due to expansion or contraction. Flexible lead wires attached to the lugs were placed as nearly as possible on the axis of the solenoid. The wooden holder could be moved back and forth along the axis of the solenoid and was marked so that the same position was obtainable every time. The method of measuring the change in resistance was essentially a potentiometer method. A known current (about 0.3 amp.) was passed

[5] Tutton, Crystallography, I, p. 138, p. 683; Ogg. Phil Mag. (6) **42,** 163 (1921); James Phil. Mag. (6) **42,** 193 (1921); McKeehan, Jour. Frkl. Inst. **195,** 59 (1923).

[6] James, Ref. 5.

[7] Bridgman, Proc. Am. Acad. of Arts and Sci. **60,** 305 (1925); 61, 101 (1926).

[8] Grüneisen and Goens, Zeits. f. Physik **37,** 378 (1926).

[9] Linder, Phys. Rev. **29,** 554 (1927).

[10] Boydston, Phys. Rev. (2) **30,** 911 (1928).

through the crystal and set up a potential difference between its ends. This potential difference was balanced in an auxilliary circuit. The value of a certain resistance, R, in this circuit with zero magnetic field was observed and this constituted a zero reading. With the field on R had to be increased to R'. The ratio, R'/R, is equal to the ratio $(r+\Delta r)/r$, where r is the crystal resistance and Δr is the increment in resistance. Computation of $\Delta r/r$ follows obviously. Zero readings were always taken both before and after the reading for any particular field. This was necessary as a drift in the zero always occurred when the field had been on for some time. This was undoubtedly caused by temperature change in the specimen.

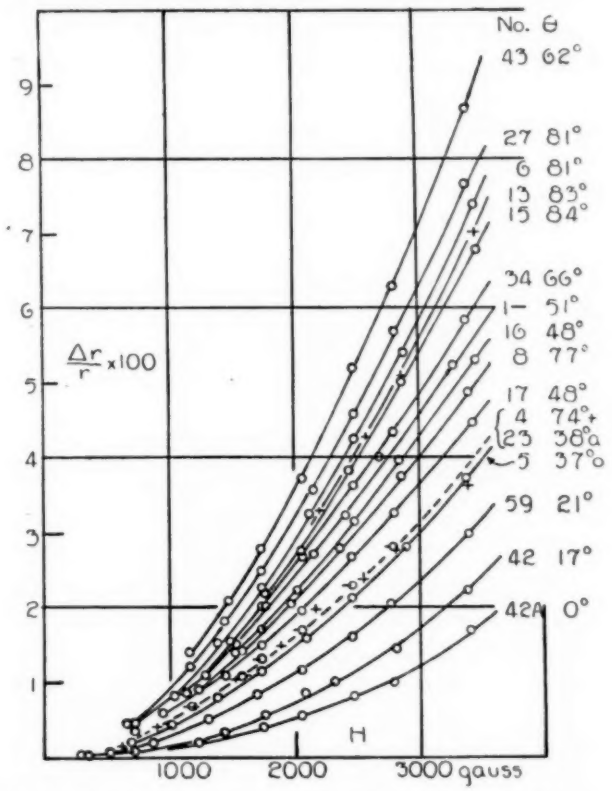


Fig. 1. Change in resistance as a function of the longitudinal magnetic field.

Results

$\Delta r/r$ as a function of the orientation. About one hundred crystals were made with an orientation varying from 17° to 90°, and of these sixty-two were used. While in general it was possible to make crystals of most of the desired orientations by growing from a single parent crystal placed in the melt at the appropriate angle, difficulty was experienced in producing those with very low orientations.

Fifteen of the crystals were measured for nine different values of H up to 3480 gauss, and readings were taken on the rest for three or four field

strengths. The results for these fifteen are shown graphically in Fig. 1. It seems likely from various theories of galvano-magnetic effects that $\Delta r/r$ should be a parabolic function of the field strength. This has been found to be approximately true by other investigators and is found to be roughly true for all orientations in the present work.

Assuming the relation:

$$\Delta r/r = AH^z \tag{1}$$

where A and z are constants, a plot between $\log \Delta r/r$ and $\log H$ should yield a straight line whose slope is the constant, z. All the curves of Fig. 1 have been plotted to such a logarithmic scale and the points do fall upon straight lines, at least for field strengths above 1000 gauss. For lower fields some of the lines show an appreciable curvature, the slope increasing with decreasing H. The values of z obtained from the straight line portions of the curves are shown in Table I. With three exceptions, they are all notably

TABLE I

Values of z in the relation $\Delta r/r = AH^z$

Crystal No.	Orientation (degrees)	z	Crystal No.	Orientation (degrees)	z
42B	0	2.10	43	62	1.71
42	17	2.24	34	66	1.75
59	21	1.94	4	74	1.57
5	37	1.83	8	77	1.62
23	38	1.57	27	81	1.72
16	48	1.64	6	81	1.82
17	48	1.59	13	83	1.78
1	51	1.75	15	84	1.78

under 2, but there seems to be no consistent variation with orientation angle or magnitude of resistance change, except perhaps for the three lowest orientations. These are likewise the orientations which show the smallest change in resistance.

It can be seen from curves in Fig. 1 that the magnitude of the resistance change, for any field, does not increase continually with increasing orientation, since in many cases curves of higher orientation are below those of lower orientations. What seems at first to be mere inconsistency turns out to be a remarkably critical variation of the effect with orientation. This relationship is depicted in the curve of Fig. 2(a), in which are plotted observations at 3480 gauss on all the 62 crystals. While it is true that the points are scattered to an extent presumably beyond the probable error of the observations it seems likely that the general trend gives maxima at approximately 62° and 80°, and minima at 0°, 73°, and 90°. It must be remembered that the different points represent entirely independent observations taken on different crystals with many different parent crystals.

It is realized, of course, that the curve as drawn beyond about $\theta = 50°$ needs considerable defense. There are only three points to establish the maximum at $\theta = 62°$. However, if the observed values of these three points

are really as much as 0.02 too high, which is about the largest difference in $\Delta r/r$ values observed for any crystals of the same orientation, the maximum at 62° would still exist, though it would not be as pronounced as it is shown. Of the points between 70° and 74°, three are far above the curve, but there seem to be enough low points in this region to justify the curve as drawn. The maximum at 80° is considered to be established by the five high points at 80°–81°, with no low points exactly at this orientation and only one neighboring high point ($\theta=76°$, $\Delta r/r=0.078$) with about the same value of $\Delta r/r$. From 85°–90° the points are very much scattered, but there is no doubt that the average value of $\Delta r/r$ for them is less than the corresponding quantity for the interval $\theta=79°$–$82°$. It may be said that it is not believed

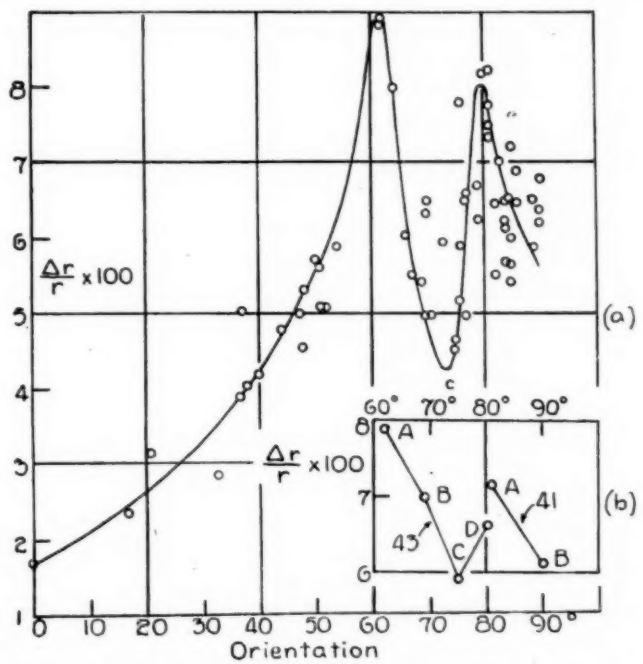


Fig. 2. Change in resistance as a function of orientation for a constant field: (a) Crystals measured as grown, $H=3480$ gauss; (b) Modified crystals, $H=3330$ gauss.

that the scattering is due to experimental error, although the angle measurement is accurate to only about 1°, which, of course, is rather serious in the neighborhood of a sharp maximum or minimum. The measurement of $\Delta r/r$ is believed to be accurate to one percent of the plotted values, since crystals could be taken out of the holder, resoldered and remeasured with results differing only by that amount. It may be mentioned also that both van Everdingen and Borelius and Lindh report values of $\Delta r/r$ for some intermediate orientations (60° and 45°, respectively), which are higher than the $\Delta r/r$ values for 0° and 90°. This gives some confirmation of the first maximum ($\theta=63$). The writer has found no data for the longitudinal effect in the neighborhood of $\theta=80°$.

Of course, the curve of Fig. 2 will be repeated (as a mirror image) if the angle of orientation is extended above 90°, in which case the minimum at 90° appears even more striking, falling as it does between two maxima about 20° apart, quite similar to the minimum at 73° between the nearby maxima. A great deal of effort was given to establishing the reality of the minimum at 90°, as can be seen by the density of points above 80°. Orientations above 85° could not be measured on the spectrometer but were estimated.

The existence of maximum and minimum values for $\Delta r/r$ between $\theta = 0°$ and $\theta = 90°$ was so remarkable that it seemed desirable to have an independent check of it. Many variations can conceivably exist between apparently similar crystals made from the same melt due to slight differences in circumstances during growth, differences in handling, etc. It was, therefore, deemed advisable to measure the value of $\Delta r/r$ for the same specimen with direction of current flow in it and magnetic field in a different direction relative to the vertical axis. Within a narrow range this can be done. While it is not feasible to set up an appreciably non-axial current in a wire, it is possible to alter the axis of the wire by cutting or grinding from the surface, and so, in the case of the thicker crystals, to alter the relation between the principal axis and the direction of current flow by 10 or 15°. This experiment was actually tried. Crystal No. 41 was a thick one with an orientation of about 82°. It was measured and then split as carefully as possible along the main cleavage planes, giving a crystal with an orientation of 90°. When it was subsequently tested the value of $\Delta r/r$ was found to have decreased. This effect is shown in Fig. 2(b). For other variations in orientation it was necessary to grind instead of split the crystal. Several of the thicker crystals were treated in this manner and the results for one of them are also shown in Fig. 2(b). In this case (No. 43), the same crystal was changed in orientation by almost 20°, starting from 62°, corresponding to a large value of $\Delta r/r$. As the angle of orientation was increased, the value of $\Delta r/r$ at first decreased and later (as the angle approached 80°) increased, roughly paralleling the course of the curve of Fig. 2(a). The field used here was about 150 gauss lower than for the observations of Fig. 2(a).

Previous to this it had not been possible to make crystals of very low orientation. However, crystal No. 42 at 17° orientation happened to be a thick one and it was cut until the orientation was reduced to 0° and measured to give curve 42A in Fig. 1 and the point of zero orientation in Fig. 2(a).

Although, in the above, strains were avoided as much as possible, it was desirable to see what effect strains would have on $\Delta r/r$. To test this point several crystals were severely bent while in the holder and then remeasured. There was very little difference between the readings before and after bending.

An experiment which may throw a little more light on the significance of the results shown in Fig. 2 consisted in altering slightly the direction of the magnetic field with respect to the wire axis, to see whether the values of $\Delta r/r$ found were primarily functions of the relative orientation of the magnetic field and the crystal or of the electric field (*i.e.*, the current) and

the crystal. While of course the effect might differ very much if the magnetic field is changed from a longitudinal to a transverse direction it was thought possible that a significant change might be detected with only a small change in the field direction when working on the crystal near a critical orientation. No such changes were observed, however, with changes in the direction of the field as high as 10°. This rules out the hypothesis that the relation of the magnetic field to the crystal axis is primarily responsible for the observed effect. Even with a picture of a more or less isotropic current distribution in the absence of a magnetic field (*i.e.*, with motions of electrons in substantially all directions with the velocity of thermal equilibrium except for the drift produced by the electric field), it might still be supposed that the magnetic field could have the effect found if we supposed that at some orientations

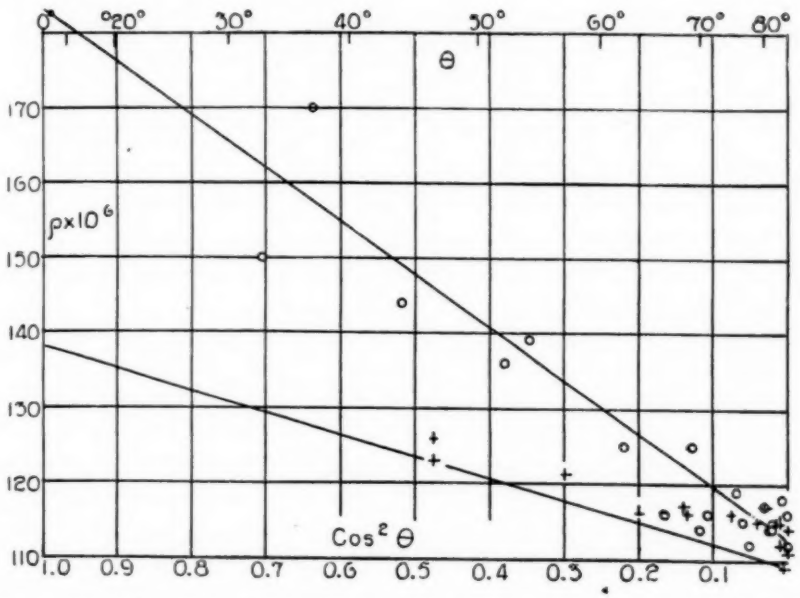


Fig. 3. Specific resistance, plotted to test Voigt-Thomson symmetry relation. The crosses represent the observations of Bridgman, the circles those of the writer.

it was able to direct electrons into atoms which would terminate their free paths and for other orientations would enable the electrons to escape those obstacles. The experiment described above seems to rule out this hypothesis.

As a further check, it was considered desirable to find out whether an effect similar to that found for $\Delta r/r$ existed in the value of the resistance itself, *i.e.*, whether the critical effect was due to the numerator or denominator of $\Delta r/r$. As the crystals were not uniform in cross section an average cross section was found by weighing and dividing by the product of the density and the length of the sample. Knowing the drop in potential across a crystal and the current through it the specific resistances could then be calculated. Naturally very accurate results cannot be obtained with these non-uniform crystals. The specific resistance, ρ, should satisfy the Voigt-Thomson sym-

metry relation. This is tested, as usual, by plotting values of ρ against $\cos^2\theta$, where θ is the orientation. Fig. 3 shows such a plot, the writer's observations being indicated by circles while observations by Bridgman[11] are indicated by crosses. In both cases a straight line may be drawn through the points though not the same line. In particular, the value of specific resistance for $\theta=0$ is quite different, Bridgman's value being considerably lower. The line for Bridgman's observations has been drawn through what he considers the most probable values of $\rho_\perp$ and $\rho_\parallel$. Although the writer's results agree with earlier observations, as shown in Table II, it must be stated that Bridgman attributes the high resistance for $\theta=0$ to the existence

TABLE II

Specific resistances of the two principal orientations.

Observer	$\rho_\parallel \times 10^6$	$\rho_\perp \times 10^6$ (ohms/cm³)	$\rho_\parallel/\rho_\perp$
Matteuci	—	—	1.60
van Everdingen	348	207	1.68
Borelius and Lindh	192	124	1.55
Bridgman	138	109	1.26
Writer	183	113	1.62

of fissures parallel to the main cleavage plane. Borelius and Lindh (ref. 4, p. 124) note also that a specimen of zero orientation has its resistance lowered by compression in the direction of the vertical axis. It is possible that the method used by the writer to prepare his crystals might produce such minute fissures since the upper portion of the crystal during growth is strained by the weight of the part below it. It must be noted, however, that this effect, if it exists, apparently does not invalidate the linear relation between ρ and $\cos^2\theta$. Further, disturbing effects would be least for crystals of high orientation (60°–90°) and it is in this region that the maxima and minima of Fig. 2 occur. It is concluded that there is no critical variation of resistance with orientation which would account for the relation between $\Delta r/r$ and orientation.

In this investigation, as stated before, the resistance change has been considered as a function of only a single variable, the orientation of the vertical axis. To define exactly the crystal position one other angle coordinate is necessary, such as the direction of one of the digonal axes with respect to the specimen axis. Hitherto it has been found that galvanometric effects (such as those following the Voigt-Thomson law) depend only on the position of the principal axis, but with a phenomenon so sensitive to angle change as the present one, it seemed likely that the direction of one of the digonal axes could not be neglected. For instance, when the principal cleavage planes are across the wire (zero orientation) a minimum effect is found; it might well be that where the minor cleavage plane $(11\bar{1})$ is exactly across the wire axis that another minimum should occur, and in fact this might well account for the minimum at about 73° orientation since the angle between these two

[11] Bridgman, Proc. Am. Acad. of Arts and Sciences **60**, 351–2 (1925).

planes has about that value. Variations in orientation of a digonal axis might also account for the scattering of the points. Consequently the experiment was tried of keeping the principal orientation fixed and varying the orientation of a minor axis (digonal) as shown by the relative position of the secondary $(11\bar{1})$ cleavage planes. Crystals could be made by suitably adjusting the angle of contact of the parent crystal before raising from the melt so that the principal cleavage planes in each case were approximately parallel while the minor cleavage plane could in successive crystals be shifted so that it made different angles with the wire axis. No change could be detected however in the value of $\Delta r/r$ which could be attributed to this change. In particular, crystals with minor cleavage planes cut exactly across the crystals[12] did not show an extremum when compared with other crystals of the same principal orientation but different minor orientations. The experiments along this line were not very extended, however, as they are somewhat difficult to control. The principal orientation, upon which the effect depends so sensitively, is especially difficult to produce exactly as desired and to measure accurately. Apparently similar crystals did not always give identical results. Moreover the range of variation in orientation of the $(11\bar{1})$ planes which could be produced was not very large. Possibly the effect of this minor orientation could be found by using a single large crystal cut into different forms.

Before the complexity of the phenomena presented at room temperature was understood, measurements were made on some of the crystals at liquid air temperatures. This work must be more thoroughly done before it can be reported upon, but it may be said that the results at low temperatures do not follow the same laws as at room temperature. This is not surprising since the effect at these low temperatures is of the order of 20 times greater than the effect at room temperature. A theory of the effect which would apply when Δr is small compared with the resistance itself will involve approximations which cannot possibly be valid when the resistance change is comparable to the initial resistance.

In conclusion the writer wishes to express his indebtedness to Professor E. P. T. Tyndall, who suggested the problem and under whose direction the work was mainly done, and to Professor J. A. Eldridge, for their ever-ready assistance and inspiration.

PHYSICS LABORATORY,
UNIVERSITY OF IOWA,
October, 1927.

[12] In general, crystals of high orientation seem most inclined to grow with the minor cleavage plane almost perpendicular to the wire axis.

EVAPORATION OF TUNGSTEN UNDER VARIOUS PRESSURES OF ARGON

By G. R. Fonda

Abstract

Theory of the mechanism of the evaporation of a tungsten filament in the presence of an inert gas.—A theory of the evaporation of a heated tungsten filament immersed in an inert gas is developed in which it is assumed that the evaporating atoms diffuse through a film of stationary gas surrounding the filament. The diameter of the film is calculated from Langmuir's equation for the heat loss from a filament. The theory leads to the relation $maP \log b/a = \text{constant}$, where m is the rate of evaporation, P is the pressure, and a and b are the diameters of the filaments and gas film respectively.

Test of the theory. Rate of evaporation of a tungsten filament at 2870°K in a gas mixture, 86% argon, 14% nitrogen.—By measuring the loss in weight of the filament the rate of evaporation for various gas pressures was calculated. The rates varied from 230×10^{-9} gr/cm² sec. in a vacuum to 2×10^{-9} gr/cm² sec. at a pressure of 165 cm. It is shown that when b is calculated from Langmuir's equation for heat loss the expression $maP \log b/a$ is actually constant for gas pressures in excess of 10 cm. The fact that the round filaments developed a hexagonal cross-section in accord with the normal crystalline shapes of tungsten grains is further evidence of the backward diffusion of evaporated metal with consequent condensation on the filament.

IN A paper published several years ago[1] the author described experiments on the rate of evaporation of tungsten filaments. These filaments varied in crystalline structure and in diameter. At constant temperature the former of these factors was found to be of marked influence both in vacuum and in the inert gases, argon and nitrogen, and the diameter was found to be of no influence in vacuum-results which were in accord with accepted hypotheses of evaporation.

In the case of the inert gases, however, a surprising feature developed, in that the diameter of the filament was found to be a noteworthy factor. The larger the diameter, the smaller proved to be the rate of evaporation. This result was explained quantitatively by the assumption that the evaporation from a filament in a gas at a pressure near atmospheric is a diffusion phenomenon within a certain limited range of distance from the filament's surface. In his theory for the heat loss from incandescent wires in gases, Langmuir has conceived[2] that the filament is surrounded by a stationary cylindrical film of gas through which the heat from the filament is carried purely by conduction. The assumption of the existence of such a film of the same dimension was found to be also useful in explaining the mechanism of evaporation. The filament was considered to be surrounded by tungsten

[1] G. R. Fonda, Phys. Rev. **21**, 343 (1923).
[2] I. Langmuir, Phys. Rev. **34**, 406 (1912).

vapor at the same pressure as would be present in a vacuum. The atoms of this vapor, however, instead of being projected directly from the filament, as in a vacuum, were pictured as diffusing through the stationary film of gas. Once an atom reached the outer boundary of the film, it would be carried away in the convection current of gas and would be lost to the filament; but the path within the film was so irregular that an atom might in fact return to the filament and be deposited on it, thus leading to a reduced evaporation as compared with that in a vacuum.

The results of the tests at constant pressure of gas and temperature of filament were found to fit the empirical expression, $m\ a \log b/a = \text{constant}$, where m is the rate of evaporation from the filament, a the diameter of the filament, and b the diameter of the gas film, calculated from the Langmuir equation.

As the filament increases in diameter, the value of b likewise increases somewhat. For such a case the expression is in accord with a decrease in the rate of evaporation, and it is obvious that an increase in either a or b should increase the chance of an irregularly diffusing atom of tungsten colliding once more with the filament.

Another test of this hypothesis is to vary the pressure of gas and note whether the expression still remains constant. In this case the diameter of the stationary gas film increases as the pressure is diminished—a change favoring a still lower rate of evaporation by allowing a greater chance for the return of evaporated atoms to the filament. This however is more than counteracted by the fewer collisions between tungsten atoms and molecules of gas—a change which allows of a more ready and direct diffusion of the former through the film of gas. The present experiments have been made in various pressures of argon to test the validity of this hypothesis. The course of the diffusion in such a case can be derived as follows and an expression obtained similar to the empirical one already described.

For the diffusion of tungsten atoms through a gas, $dq/ds = D\,dc/dr$, where dq is the number of atoms passing through area ds, dc/dr is the concentration gradient of tungsten atoms in a direction at right angles to ds, and D is the diffusion coefficient in the gas. If this diffusion is uniformly distributed over the area s, $q = Dsdc/dr$, or, for the diffusion from a wire through an area of surrounding gas having unit length,

$$q = D\,2\pi r dc/dr. \tag{1}$$

The Meyer formula for the diffusion of two gases,[3] expressed in terms of the atoms of tungsten vapor (W) and the molecules of argon gas (A) involved here, is

$$D = (1/3n)(u_W l_W n_A + u_A l_A n_W)$$

where u is the root mean square velocity, l the mean free path, and n the number of molecules per cc.

[3] Meyer, Kinetische Theorie der Gase, 1895, Art. 95.

At a constant filament temperature of 2870°K, at which the tests were made, n_W is negligibly small (corresponding to a pressure of 0.000017 mm),[4] compared with n_A, so that n, the total number of molecules per cc, is virtually equal to n_A, and the second term falls out, giving the expression $D=(1/3)u_W l_W$.

The velocity of tungsten atoms is a function of filament temperature and is therefore likewise constant in these tests.

As the mean free path of the tungsten atoms is dependent on the pressure of the argon, their coefficient of diffusion is inversely proportional to the pressure P and Eq. (1) becomes $q=(2\pi r/P)dc/dr$, and this integrated gives

$$(1/2\pi)\int dr/r=dc/qP\,.$$

For wire of diameter a and gas film of diameter b, calculated as before from the Langmuir equation for heat loss,

$$(1/2\pi)\int_{b/2}^{a/2} dr/r=(1/2\pi)\log b/a\,.$$

Furthermore if m is the rate of evaporation per unit of surface, $q/2\pi a$, then

$$maP\log b/a=\int dc=c_a-c_b=\text{constant} \qquad (2)$$

where c_a and c_b are the concentrations of the tungsten atoms at the surface of the filament and at the surface of the gas film, respectively. These concentrations are constant because in a case like this, where the filament burns at a constant temperature in argon at various pressures, it is assumed that the diffusion of tungsten atoms is the only variable and that the concentration of tungsten vapor is constant at the outer border of the gas film, regardless of the pressure, just as it is at the surface of the filament, where it is determined of course by the vapor pressure. These assumptions are borne out by the experiments.

In the experiments the filaments were of a constant diameter of 0.00978 cm and bent into a hairpin shape, having a total length of 12 cm. They were all set up initially at a constant temperature, as determined by color match, of 2870°K on the Worthing and Forsythe temperature scale[5], and were then burned at constant voltage. The rate of evaporation was determined from the loss in weight and was calculated from Langmuir's equation[6]

$$m=(\rho/\pi)^{1/2}(w_i^{1/2}-w_f^{1/2})/t$$

where ρ is the density of tungsten, 19.3; w_i and w_f are the initial and final weights of the filament in gr/cm; and t is the time in seconds.

[4] Jones, Langmuir and Mackay, Phys. Rev. **30**, 211 (1927).
[5] Worthing and Forsythe, Astrophys. J. **61**, 146 (1925).
[6] Langmuir, Phys. Rev. **2**, 329 (1913).

The gas used was a mixture of 86% argon and 14% nitrogen, such as is used at present in gas-filled lamps. It was introduced to the lamps at various pressures, as noted in the table. The values recorded are the averages of several tests made at different times, all in good agreement with one another. Each test was itself an average taken from measurements of six lamps which had been treated simultaneously.

A pressure of two atmospheres was attained by having a supplementary bulb attached to the lamps and sealing both off as a unit at a pressure of 700 mm. The lamp was then immersed in liquid air to condense some of the

TABLE I

Rate of evaporation of tungsten in 86% argon, 14% nitrogen at 2870°K.
Diameter of filament = 0.00978 cm.

Press (cm)	Rate Evap. $m(10)^9$	b (cm)	$maP \log b/a \times 10^9$	$m/b \times 10^9$
0	230	—	—	—
1	57.5	9.68	3.9	—
5	23.5	2.42	6.3	—
10	20.5	1.31	9.8	15.6
25	10.3	0.63	10.4	16.2
50	5.4	0.36	9.6	14.8
70	4.2	0.28	9.6	14.8
165	2.0	0.15	8.8	13.5

mixture and the supplementary bulb sealed off. Examination of the gas in the latter allowed of determination of the pressure in the lamp. This operation led of course to a slight enrichment of the argon in the lamp, amounting to about 3%, sufficient to reduce the rate of evaporation 1.5%. Allowance is made for this in the table, so that all values recorded are for the one composition of 86% argon.

These values are plotted on the curve of Fig. 1. They hold only for wire of this specific diameter, because, as already noted, filaments of a larger size have lower rates of evaporation in gas.

In the case of the tests in vacuum, the value found experimentally of $230\ (10)^{-9}$ is in good agreement with that of $250\ (10)^{-9}$, as given by Jones, Langmuir and Mackay.[4]

The expression $maP \log b/a$ is sufficiently constant at pressures above 10 cm to allow of credence being given the hypothesis developed above.

The constancy of the expression has a further significance, for, as is evident from its derivation, it denotes a constant difference between the vapor pressure of tungsten at the surface of the filament and at the surface of the film of gas. For constant filament temperature this implies that the concentration of tungsten vapor at the surface of the stationary film of gas should be constant for all pressures above 10 cm. It is this vapor which constitutes that which effectively evaporates from the filament, for the rising convection currents of gas carry it off to be deposited on the bulb. The rate of evaporation at different pressures should be determined therefore by the area of the assumed film of gas if the concentration of vapor at its border is

in fact a constant. As a criterion of this, values of m/b are given in the last column of the table. It is evident that this expression is sufficiently constant for pressures of 10 cm and above to render the hypothesis credible.

The rate of evaporation in 86% argon 14% nitrogen at 50 cm pressure is 2.3% of that in vacuum at the temperature of 2870°K and for this size of wire. Other experiments have shown that at 2720°K it is a still smaller percentage of the rate in vacuum—in other words, the vapor pressure of tungsten at the boundary of the film of stationary gas is smaller proportionately to the vapor pressure at the filament surface. More of the tungsten evaporating evidently returns to the filament as its temperature is reduced, no doubt because of the greater density gradient of the argon.

For pressures below 10 cm the hypothesis developed above breaks down for obvious reasons, as the diameter of the stationary film of gas becomes

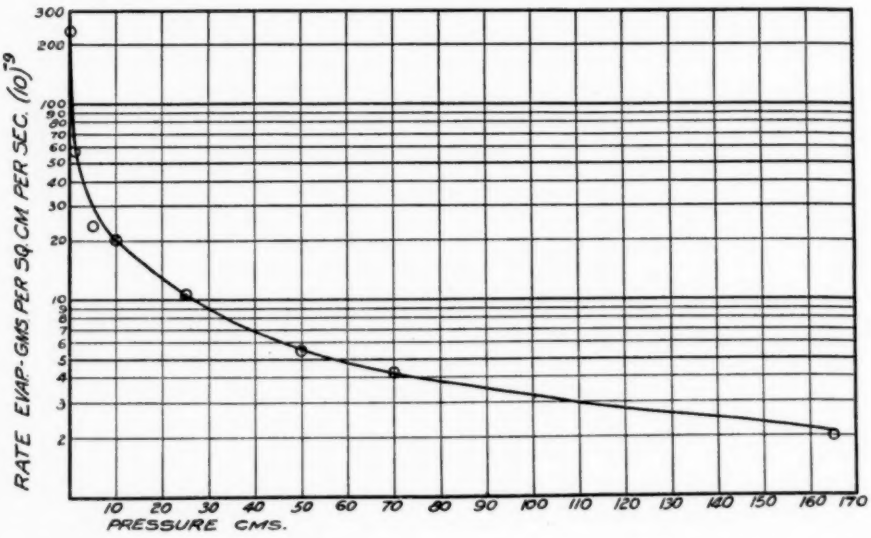


Fig. 1. Rate of evaporation of tungsten in a gas mixture, 86% argon, 14% nitrogen for various gas pressures. Temperature of filament 2870°K, diameter of filament 0.00978 cm.

greater than that of the bulb. Another relationship quite evidently should hold here. One has been developed by Weber[7] and applied to experiments by Oosterhuis which calls for proportionality between the rate of evaporation and the square root of the gas pressure. Although it does not hold as well at higher pressures as the expression developed above, it gives such agreement at the range of low pressures as to warrant consideration for expressing the mechanism of evaporation in cases where there are no convection currents of gas.

The appearance of the filaments bore testimony to the assumption that the evaporation from them had been a diffusion phenomenon. They had all

[7] Weber, Handelingen van het XVI Nederlandsch. Natuur en Geneeskundig Congres, 1917, p. 102.

been taken from the same spool of non-sag tungsten wire, which has the characteristic of developing long grains in the process of grain growth accompanying heating of the wire. When tested in a vacuum this wire was found to remain uniformly round throughout its life. The filaments tested in gas, however, were found to have become approximately hexagonal in cross-section. The hexagonal cross-section was more perfectly developed at the lower temperature of 2720°K, where, as already shown, deposition is still more marked.

Such filaments are similar in appearance to those single crystals of tungsten described by vanArkel[8] which he had prepared by heating a single crystal of tungsten in the presence of tungsten hexachloride vapor. The latter was decomposed and its tungsten content deposited on the filament, but in such a manner that the originally round filament became coated with a deposit whose cross-section was hexagonal.

In the case of the experiments described herein on filaments heated in argon, there has evidently been a similar action, except that the deposit, instead of coming from an extraneous source, is made up of atoms which have been carried away from the filament by evaporation and have then returned to it again by the process of diffusion. In this return those atoms which adjust their position to the orientation of the crystal on which they fall are more strongly held than those whose orientation is different. The latter therefore evaporate again more readily and the result is the formation of a cross-section in accord with the normal crystalline structure of the metal. As Langmuir says in a discussion of what he terms "reversible sublimation," in accounting for the ability of condensing atoms to arrange themselves to form a crystalline unit:[9] "The continual evaporation and condensation going on over the whole surface of the crystal allow the atoms to arrange themselves in the most stable position."

This mechanism explains satisfactorily the change from a round to an hexagonal cross-section without the necessity of assuming that it is due to a difference in vapor pressure on the different faces. In fact, when a filament prepared by the vanArkel process was tested in vacuum at a temperature of 2720°K until it had lost about 30% in weight and failed by burn-out, its cross-section was still hexagonal, with the angles between faces just as sharp as initially.

These data on the variation in rate of evaporation with pressure of argon are of value in calculating the lives of gas-filled lamps. The other factor involved is the heat loss through the gas which determines the temperature of operation. The fact that the rate of evaporation increases for pressures below atmospheric does not necessarily mean that the life of lamps at constant efficiency decreases correspondingly. If the effective diameter of the filament is so small that the heat loss is relatively large, then a reduction in pressure may so decidedly lower the heat loss and consequently the operating

[8] van Arkel, Physica **3**, 76 (1923).
[9] I. Langmuir, Jour Amer. Chem. Soc. **38**, 2253 (1916).

temperature that the rate of evaporation will actually be reduced. Such a condition existed in the early low wattage lamps whose filament was of such sagging wire that it had to be wound on a small mandrel to retain its shape during operation. For such a lamp a maximum life was calculated for a pressure of one-half atmosphere and was confirmed by test. With the advent of non-sag wire, the filaments of gas-filled lamps could be given such large effective diameters that both calculation and test are in agreement in showing a continuous increase in life with increase in pressure for all sizes of lamps.

The writer wishes to express his gratitude to Miss Amy Walker for her assistance in the experiments and to Dr. Langmuir for his interest and criticisms.

RESEARCH LABORATORY,
GENERAL ELECTRIC COMPANY.
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EFFECT OF FREQUENCY ON THE END CORRECTION OF PIPES

By S. Herbert Anderson and Floyd C. Ostensen

Abstract

Using Blaikley's method, the end corrections of "closed" pipes have been determined for pipes of brass, with walls 0.12 cm thick and the inside diameter 9.92 cm, 7.36 cm and 4.84 cm respectively, over a range of frequencies from 128 vps to 1715 vps, and over a range of λ/D (wave-length/diameter) from 27 to 4. An electrical detector was used for determining the resonance peaks, which makes this work ten times more accurate than any formerly reported. The highest frequency used with each pipe was the limiting frequency for which resonance could be obtained, and in each case was such that $\lambda/D=4$ approximately.

The end correction was found to be dependent upon the frequency, increasing with decreasing values of λ/D to $\lambda/D=6$ approximately, beyond which there was a decrease. The results indicate that when a pipe is used as a generator of a complex tone, (1) there is a limit to the number of partials which is determined by the value of λ/D for prime, (2) the higher proper tones will in some cases be sharp, but generally flat of the harmonic series, and that the corresponding partials will be of low intensity depending upon the amount of forcing required to bring them into the harmonic series.

Introduction

IT IS well known that narrow pipes used for the production of sound have a retinue of partials larger than wide pipes. One reason generally assigned for this difference is that the "end correction" apparently becomes smaller[1] as the wave-length approaches the diameter of the pipe, so that the higher proper tones are sharper than the corresponding harmonics of the fundamental tone. The bases for this statement, theoretical and experimental are not very convincing.

Theoretical treatment of the end correction of pipes has been given by Helmholtz[2] and by Rayleigh.[3] The former found a rigorous solution for a pipe that was *nearly* cylindrical. If R is the radius of the open end, the pipe is practically a cylinder of radius R throughout the greater part of its length, but bulges slightly at a distance $0.54R$ from the mouth. He also assumes, (1) that the mouth is fitted with an infinite flange, and (2) that the wave-length is large compared to R. He finds the end correction under these conditions to be $\pi R/4$. By a different method Rayleigh computed the end correction of a true cylinder, but subject to the same restrictions, and found it to be $0.82R$.

In practice both these restrictions are violated. Pipes are seldom, if ever, fitted with flanges, and while the diameter of the pipe is generally small

[1] Barton, "Textbook of Sound," Macmillan, 1908, p. 253; Crandall, "Theory of Vibrating Systems and Sound," Van Nostrand, 1926.

[2] Helmholz, Crelle-Borchardt, Journal f. Mathematik, 57, 1 (1860).

compared to the wave-length of the first mode of vibration, for higher modes the quarter-wave-length may approximate the diameter of the pipe. In this case the reflection from the open end must be quite different from that for longer wave-lengths.

As the unflanged pipe is not amenable to theory, we must depend alone on experiment for information of the end corrections of practical pipes. From his own work[4] and that of Bosanquet,[5] Rayleigh concludes that this is $0.6R$ for wave-lengths large compared to the diameter of the pipe. The effect of shorter wave-lengths was not tested. At an earlier date rather extensive work was done by Wertheim[6] and Zamminer.[7] The former found a mean value for open pipes of $0.663R$ and for closed (open at one end only) of $0.746R$, and not much variation with wave-length. On the other hand Zamminer found the end correction to decrease with decreasing values of λ/D. These results cannot be considered very reliable as in both cases the pipes were made to sound by blowing a jet of air across the open ends. Under such conditions the frequency obtained depends somewhat on the shape and velocity of the air jet and the reflection is quite different from that occurring at an undisturbed open end. Bosanquet[8] also found the correction to be dependent upon the wave-length, but the larger correction is for small values of λ/D. He considers his best values for the end correction to be $0.635R$ for $\lambda/D=6$ and $0.543R$ for $\lambda/D=15$ with open pipes. In his work the vibrations were started by a jet of air and the pitch determined after the jet was stopped as the sound died away. He estimates his error to be about 7 percent.

The best experimental work heretofore done was by Blaikley.[9] His method consisted in finding the shortest resonant length L_1 of a closed pipe when forced to vibrate by the action of a tuning fork, and the next longer resonant length L_2. Then the correction is given by

$$c=(L_2-L_1)/2-L_1 \tag{1}$$

His range of λ/D was small, from 13 to 26, and he found no great variation, the mean value being $0.576R$ with a brass tube 5.3 cm in diameter.

In view of the discrepancies of this earlier work it seemed wise to attempt another determination of the end correction over a wide range of wave-lengths and with some improvements in method.

Method

The experimental procedure was essentially that of Blaikley. The pipe was mounted vertically with the open end at the top and the length of the vibrating air column was altered by letting water in or out at the bottom. A glass gauge tube 3.3 cm inside diameter was set parallel to the pipe and

[3] Rayleigh, Theory of Sound, vol. 2, 2nd Ed., Macmillan, App. A (1926).
[4] Rayleigh, Phil Mag. (5) **3**, 456 (1877).
[5] Bosanquet, Phil. Mag. (5) **4**, 219 (1877).
[6] Wertheim, Ann. d. chimie et d. physique (3) **31**, 394 (1851).
[7] Zamminer, Pogg. Ann. d. physik u. chemie **97**, 183 (1856).
[8] Bosanquet, Phil. Mag. (5) **4**, 219 (1877).
[9] Blaikley, Phil Mag. (5) **7**, 339 (1879).

connected at the bottom to the same water intake. The level of the water was read on a scale on the back side of the gauge tube. The water reservoir was raised and lowered by a windlass so designed that the level in the pipe could be changed by as small an amount as 0.05 cm. Three sizes of brass pipes were used, 9.92 cm, 7.36 cm and 4.84 cm inside diameter respectively. In all three pipes the thickness of the wall was 0.12 cm.

The tuning fork which was electrically driven was mounted 7 to 10 cm above the open end of the pipe. Three types of drives were used: (1) the door-bell type of interrupter for forks of frequencies 128 to 384 vps; (2) a microphone button interrupter for frequencies from 512 to 1152 vps; (3) a thermionic tube drive for frequencies above 1152 vps. The position of the fork (if more than 7 cm above the opening of the pipe) and the form of the drive were found to have no effect on the end correction with the two larger pipes, but did with the smaller as will be discussed later.

Since the ear is very insensitive to small changes of intensity of sound, an electrical detector was designed for determining the peaks of resonance in the pipes. A Koenig resonator, tuned to the frequency of the fork, was suspended so that its mouth was about 5 cm to one side of the opening and a little above it. This was connected by a piece of tubing to a Magnavox loud speaker, used as a generator. The e.m.f. from the loud speaker was stepped up by a transformer, the secondary of which was connected to the grid circuit of a C-301 thermionic tube, used for amplification. The plate circuit was connected to the primary of an audiofrequency transformer, and the secondary of the same was connected through a carborundum crystal rectifier to a galvanometer. With this device a change in intensity of sound due to a change in water level in the pipe of 0.05 cm in the vicinity of the maximum of resonance could be detected. With the ear alone a change in water level of 0.5 cm was necessary to produce a noticeable change in intensity.

Sources of Error

Blaikley in his work takes account of four sources of error: (1) position of the fork; (2) temperature changes; (3) capillary action of the water in the pipe; (4) humidity. In addition to these three other possible sources of error were considered by us: (5) the stationary wave-pattern in the room; (6) resonance in the walls of the pipe; (7) action of the Koenig resonator in loading the pipe.

1. *Position of the fork.* As noted above, with the two larger pipes the position of the fork had no effect on the end correction unless it was closer to the open end than 7 cm. Neither did the form of the drive have any effect. But with the smallest pipe it was found that for two different frequencies, 512 and 1152 vps respectively, the end correction was 0.15 cm greater with the microphone drive than with the thermionic tube drive. This was accounted for by the greater area of the framework of the former, which was about four times that of the latter. From these relations it was estimated that, if it were possible to obtain resonance with the fork at a very great distance from the mouth of the pipe, the end correction would be

less by 0.2 cm for the microphone drive and 0.05 cm for the other two which had about the same area. All these measurements were with the fork 7.8 cm from the opening. Increasing the distance somewhat reduced the end correction, but this was harder to determine accurately because at great distances resonance was not great enough. Blaikley found the effect of the fork in his work by blowing jets of air across two pipes of exactly the same length and diameter with the fork mounted over one of them. Under these conditions beats could be heard between the two pipes. This was tried in our work, but no beats could be detected with the fork at the distance used. If the fork was lowered to within 3 cm of the opening, slow beats were heard. Probably Blaikley mounted his fork at this distance or less.

2. *Temperature changes.* A temperature change occurring between the measurements of the two resonance lengths would affect the observations in two ways: (1) by causing a change in the velocity of sound, and (2) by causing a change in the frequency of the fork. But if the temperature change were no greater than 0.5°C, the error would be small compared to other observational errors. No data were retained of readings taken with greater temperature variations than this. To be sure, some error would be introduced if the observations were made at a temperature other than that at which the fork was rated, since the results show that the end correction is a function of the frequency. But a simple calculation shows this to be negligible for a temperature change of 0.5°C.

3. *Capillary action.* Capillary action is negligible in pipes of the size used in this experiment.

4. *Humidity.* Variations in humidity would affect the end correction in the same way as temperature changes, by causing a change in the wave-length. The change in wave-length due to a change in humidity of a most extreme character, from absolutely dry air to saturation at 20°C, is 0.5 percent. Unless such a change occurred between the observations of the two resonant lengths (which was not the case) the error in the end correction due to humidity was negligible.

5. *The stationary wave-pattern in the room.* The effect of this was tested by placing absorbing material on the wall of the room nearest the pipe. This caused a change in reflection and hence a change in the stationary wave-pattern. No difference in the end correction was observed under the two conditions.

6. *Resonance in the walls of the pipe.* This was tested with the smallest pipe by clamping a lead ring weighing 1.2 kg at the antinode. This was tried at frequencies of 512, 640, 1280 and 1408 vps, respectively, with negative results.

7. *Action of the Koenig resonator in loading the pipe.* The loading effect of the resonator was negligible as is shown by the fact that changing the position of the resonator with reference to the pipe had no noticeable effect on the end correction obtained, although of course it did influence the magnitude of the galvanometer deflection. Furthermore, in the course of the work the apparatus was dismantled and reassembled. At no time was an exact

measurement made of the position of the resonator, and in the second set-up it was put only *approximately* in the former position. Yet the values of the end correction taken on the reassembling of the apparatus agreed with the first results as well as the individual readings between each other.

Finally, the end corrections taken at different times show the order of accuracy of the work. For the pipe 9.92 cm in diameter, the maximum deviation[10] of any end correction from the mean was 0.06 cm and the average deviation was 0.022 cm; for the 7.36 cm pipe the maximum was 0.05 cm and the average 0.024 cm; for the 4.84 cm pipe the maximum was 0.05 cm and the average 0.025 cm.

TABLE I

Resonance lengths and end corrections for brass pipes of various diameters.

	Pipe 9.92 cm in diameter					Pipe 7.36 cm in diameter					Pipe 4.84 cm in diameter					
n	L_1	L_2	c	Av. c	c/R	L_1	L_2	c	Av. c	c/R	L_1	L_2	c	Av. c	C^5	C/R
128	64.12[1]	198.52	3.08	2.95	0.59											
	64.52	198.62	2.53													
	64.02	198.52	3.23													
256	30.78	98.30	2.98	2.99	0.60	31.45	98.70	2.18	2.19	0.60	32.42	100.34	1.54	1.53	1.48	0.61
	30.75	98.24	3.00			31.44	98.71	2.20			32.04	99.14	1.51			
384	19.30	64.04	3.07	3.03	0.61	20.26	65.18	2.20	2.21	0.60	20.91	65.79	1.53	1.51	1.46	0.60
	19.20	63.56	2.98			20.24	65.15	2.22			20.90	65.68	1.49			
512	13.70	47.20	3.05	3.03	0.61	14.36	47.43	2.18	2.23	0.61	15.08	48.64	1.70	1.70	1.50	0.62
	13.75	47.25	3.00			14.31	47.46				15.11	48.71	1.69			
640	10.34	37.35	3.17	3.16	0.63	11.04	37.90	2.39	2.39[9]	0.65	11.78	38.74	1.70	1.69	1.49	0.62
	10.37	37.39	3.14			11.03	37.91	2.41			11.82	38.80	1.67			
768	8.75	31.65	2.70	2.64	0.53	8.95	31.53	2.34	2.39[9]	0.62	9.52	31.97	1.71	1.70	1.50	0.62
	8.87	31.77	2.58			9.01	31.54	2.26			9.54	31.97	1.68			
832	7.75	28.63	2.69	2.69	0.54	8.12	28.83	2.24	2.22	0.60						
	7.75	28.63	2.69			8.16	28.87	2.20								
838	7.55	48.58[4]	2.71	2.70	0.54											
	28.08[5]	69.10[6]	2.69													
853.3	7.58	27.75	2.51	2.55	0.51	7.95	28.21	2.18	2.16	0.59						
	7.50	27.65	2.58			7.95	48.29[7]	2.14								
896	7.35	26.65	2.30	2.29	0.46	7.44	26.67	2.18	2.18	0.59	7.78	27.00	1.83	1.79	1.59	0.66
	7.35	26.60	2.28			7.45	26.69				7.83	26.98	1.75			
1024						6.27	23.18	2.19	2.16	0.59	6.59	23.42	1.83	1.80	1.60	0.66
						6.29	23.13	2.13			6.61	23.34	1.76			
1115						5.60	21.12	2.16	2.14	0.58						
						5.60	21.02	2.11								
1152						5.28	20.22	2.19	2.24	0.61	5.61	20.64	1.91	1.86	1.66	0.69
						5.24	20.27	2.28			5.67	20.63	1.81			
1280											4.91	18.28	1.78	1.80	1.75	0.72
											4.86	18.22	1.82			
1408											4.15	16.04	1.80	1.82	1.77	0.73
											4.14	16.07	1.83			
1536											3.72	14.60	1.72	1.71	1.66	0.69
											3.71	14.51	1.69			
1664											3.46	13.77	1.70	1.65	1.60	0.66
											3.54	13.81	1.60			
1715											3.27	13.24	1.72	1.75	1.70	0.70
											3.24	13.26	1.77			

[1] Resonance lengths and corrections expressed in cm.
[2] Average of six measurements.
[3] Average of three measurements.
[4] Third resonant length.
[5] Second resonant length.
[6] Fourth resonant length.
[7] Third resonant length.
[8] Correction with fork at great distance from opening.

[10] Except for frequency of 128 vps for which resonance was weak.

Results

The data taken and the end corrections computed are shown in Table 1. The variation of the end correction with frequency is well shown in the curves of Fig. 1. In plotting these curves the points were weighted according to the deviations between the values averaged for a given point and the curves drawn as smooth as was consistent with this weighting. The range of frequencies used extended from the lowest frequency which is generally employed with an actual organ pipe of the same diameter as the brass pipe used in the experiment up to the highest with which a distinct resonance could be obtained. It will be observed that for each of the three pipes there is a progressive increase in the end correction from the lowest frequency up to a certain point beyond which there is a decrease. This decrease is greatest with the largest pipe and becomes smaller with a decrease in the diameter of

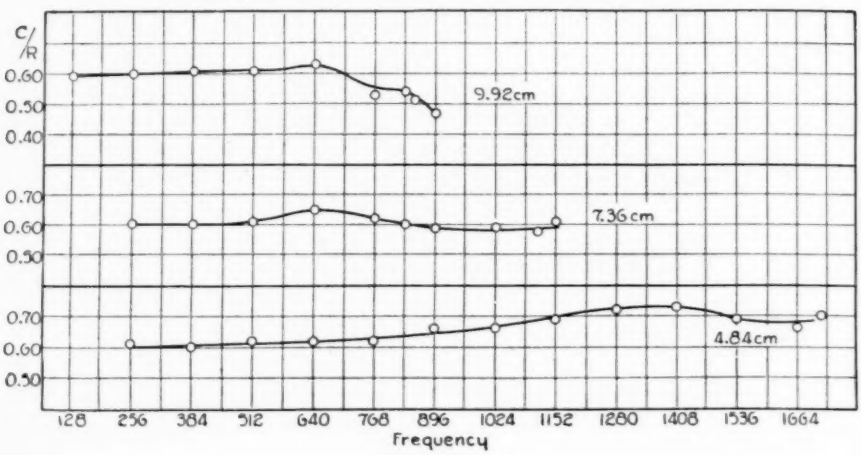

Fig. 1

the pipe, so that for the smallest one this minimum is still greater than the end correction at the beginning of the curve. The maximum correction occurs at such a frequency that λ/D is about 6. This is better shown in Fig. 2 in which the end corrections are plotted against D/λ. A scale of λ/D is laid off along the axis of abscissas.

With each pipe the highest frequency at which resonance could be obtained, and hence the end correction determined, was such that λ/D was about 4. This fact has an important bearing on the maximum number of partials that may be expected from a pipe of given *scaling* (D/λ for the prime) when used as a generator of a complex tone. If an organ pipe were designed with the diameter of the largest pipe used in this experiment, 9.92 cm, the frequency of the prime tone would be about 128 vps for a fairly large scaling of 1/27. If, as this work indicates, no proper tone can be produced whose frequency is higher than that corresponding to $\lambda/D=4$, then the partial of highest frequency will be the seventh, frequency 896 vps. Hence no more than seven partials would be expected with an open pipe of such scaling,

and with a closed pipe the seventh would be the highest of the odd-numbered partials.

The effect of the variation of the end correction with frequency and with the size of the pipe should also be considered. Taking the largest pipe again as an example, we may compute the length of a closed pipe to sound 128 vps at 20°C by

$$128 = 34{,}400/4(L_1 + 2.95) \tag{2}$$

The frequency of the seventh proper tone would be 905 vps. This is *sharper* than the seventh harmonic by 9 vps. Hence in order to have the seventh partial present in the complex tone, this proper tone would have to be "forced" into the harmonic series. This accounts for the fact that with pipes of this scaling the seventh partial is lacking entirely or is of very low intensity. The next lower proper tone, the fifth, would be flat by 2 vps, since the end correction is larger in the neighborhood of this frequency than at 128 vps.

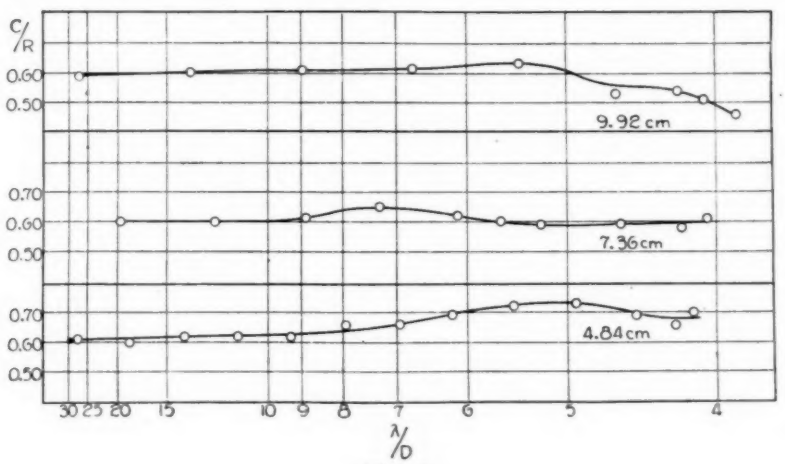

Fig. 2

Similarly the third proper tone would be flat by 1 vps. Hence the third partial is easily produced and the fifth with more difficulty. This in agreement with observations of the relative intensity of these partials in a stopped pipe of wide scaling. Hemholtz' statement[11] that, "For the wider stopped pipes, as for the wide open pipes, the next adjacent proper tones of the mass of air are distinctly higher than the corresponding upper partials of the prime and consequently these upper partials are very slightly, if at all, reinforced," is explained in terms of the variation of the end correction with frequency *only* for the seventh proper tone, since the others are flat instead of sharp.

A similar situation holds for open pipes. The second, third, fourth, and fifth proper tones will be flat of the harmonic series, the departure increasing with the number of the proper tone, while the sixth and seventh will be sharp.

If the 4.84 cm pipe were used with the same scaling, 1/27, the prime would have a frequency of about 256 vps and the highest partial possible

[11] Helmholtz, "Sensations of Tone," Longmans, Green and Co., 3rd Ed. (1895), p. 94.

would be the seventh. However the effect of the end corrections would be to make all the higher proper tones *flat* of the harmonic series, the greatest departure being for the fifth, viz., 11 vps. This in the neighborhood of 1280 vps is almost exactly the same difference in pitch as 9 vps in the neighnorhood of 896 vps. Hence, if the seventh partial is lacking in the former case, the fifth would be here. It would thus appear that, if the same scaling used in a set of pipes with a view of obtaining uniform quality of tone, *the higher partials are fewer and less prominent in the higher pitched pipes than in the lower pitched.* This point should be tested by analysis of organ pipe tones.

If the 4.84 cm pipe were used with a scaling of 1/54, as is used in the Gamba stop for example, the frequency of the prime would be about 128 vps. Under such conditions the ninth proper tone would be flat by only 2 vps and so readily forced into the harmonic series. This is in agreement with observations of small scaled pipes, such having a large retinue of partials.

Conclusions

It is recognized, of course, that there are other factors affecting the relative intensity of the partials tones of pipes, such as the material of the walls, size and shape of the mouth or embouchre, and the wind pressure of blowing. This paper considers only one factor, the effect of the end correction.

This work seems to verify the general idea that the difference in the number of partials in wide and narrow pipes is in part due to a variation of the end correction with frequency, but does not verify Hemholtz' statement that the higher proper tones of wide pipes are *sharper* than the corresponding partials of the harmonic series. Our work indicates that in general they should be *flat*. Furthermore, the end corrections are relatively larger for narrow pipes than for wide, so that for pipes of the same scaling the higher pitched ones will have fewer partials than the low pitched.

We are much indebted to Mr. P. M. Higgs for suggestions regarding the electric detector.

Department of Physics,
University of Washington,
September 13, 1927.

A SIMPLE METHOD OF FINDING THE SOUND ABSORBING POWER OF A BUILDING MATERIAL

By Gunnar Heimburger*

Abstract

An accurate method of comparing the absorbing powers of building materials is described. As in Taylor's method, a Rayleigh disk is used to examine the standing waves inside a tube, one end of which is closed by the test material. The main feature of the method is the comparison of the values of the maximum sound intensity in the standing waves when the end of the tube is closed first by a hard material and then by the material under test. The results are accurately reproducible.

Absorption coefficient at pitch 295 of various building materials.—The following values of the absorption coefficient were obtained:—commercial Celotex, 7/16″, not perforated, 0.17; acoustical Celotex, 7/8″, perforated side exposed, 0.34; J. M. Asbestos Akoustikos felt, ½″ thick, one layer, 0.15; two layers, 0.43; J. M. Akoustikos felt, 1″ thick (older type), 0.13; Akoustolith, 1″ thick, tile, 0.15; Rumford tile, 1″ thick, 0.22.

Introduction

THERE are two methods by means of which the acoustical absorption coefficients of building materials have been found. The first is the reverberation method developed by the late Professor Wallace C. Sabine of Harvard University and so largely used that nearly all the values of these coefficients which we have at our disposal have been determined in this manner. An important feature of this method is that the material being investigated covers the walls of the test room in the same way as it does under actual conditions. On the other hand, the ear must be used as the sound measuring instrument, and on account of variations of sensibility in the individual ear, satisfactory mean values are obtained only after long training and as the result of very many observations. Measurements taken by this method are accordingly rather slow and may be expensive, especially on account of the cost of preparing the test room. They may also at times yield values affected somewhat by resonance varying with the method of mounting the material.

The second method, pursued by Weisbach,[1] Taylor,[2] Wente,[3] Eckhart[4] and Chrisler, Paris,[5] and others involves using a very much smaller quantity

* Research Fellow in Harvard University from the American-Scandinavian Foundation.

[1] F. Weisbach, Versuche über Schalldurchlässigkeit, Schallreflexion und Schallabsorption, Ann. d. Physik, **33**, 763–798 (1910).

[2] H. O. Taylor, A direct method of finding the value of materials as sound absorbers, Phys. Rev., **2**, 270–287 (1913).

[3] E. C. Wente: Unpublished, see I. B. Crandall: Theory of vibrating system and sound, pp. 108–109. D. Van Nostrand Company. New York, 1926.

[4] E. A. Eckhart and V. L. Chrisler, Transmission and absorption of sound by some building materials, Bureau of Standards, Bull. 526 (1926).

[5] E. T. Paris: On the stationary wave method of measuring sound absorption at normal incidence. Phys. Soc. Proc. **39**, 269–295 (1927).

of the test material and a more quantitative measuring instrument. A tube, one end of which is closed with the material under investigation, is tuned in resonance with a steady sound source, (except that Paris uses an untuned pipe) and the absorption coefficient is found from measurements on the standing wave system inside the tube, usually by comparing the maximum energy value at an antinode with the minimum value at a node. For measuring the sound intensity Weisbach and Eckhart and Chrisler used a telephone receiver, Paris a hot wire microphone, tuned in resonance with the pitch, and Taylor a Rayleigh disk. In the actual measurements by this method the energy at a node may be a hundred times smaller than that at the antinode and may be difficult to measure with any considerable percentage accuracy. For instance, in one example given by Taylor, the result may be out by more than 25 percent if we assume that the readings of the Rayleigh disk are accurate only to 0.2 mm. Such cases are likely to arise unless the material is very absorbent, and it will be almost impossible to secure an accurate result in these cases unless we follow the procedure of Eckhart and Chrisler and amplify the minimum values. This involves a rather complicated and expensive arrangement of apparatus.

The object of this note is to present a simple method somewhat like that of Taylor, but not subject to the error mentioned above. The results are of a preliminary nature, and the method is in its present form adapted only to comparing the absorbing powers of different materials. Since the absorption coefficients are well known for several standard materials, it is not difficult to determine new ones with reference to these. The main idea of the method is to compare the values of the *maximum* sound intensity in the standing wave in the tube in the cases when the end of the tube is closed first by a hard material and then with the material under test. These values are always large enough to be accurately measurable, and with care in the experimental arrangements they may be made constant and reproducible. From these measurements the absorption coefficient can be obtained.

Theory of Absorption Measurements

Imagine a tube with non-absorbing walls and an absorbent end, and let the absorption coefficient for the closed end of the tube be a. Then $(1-a)$, the reflection coefficient, is the ratio of reflected to incident energies, and the square root, $(1-a)^{1/2}$, is the ratio of reflected to incident amplitude. In the standing wave-system the amplitude at an antinode is equal to the sum of the amplitudes in the incident and reflected waves, and the amplitude at a node is equal to the difference of the amplitudes. Since the energy is proportional to the square of the amplitude, we have the ratio of energy at an antinode to energy at a node:

$$\frac{\text{Energy at antinode}}{\text{Energy at node}} = \frac{[1+(1-a)^{1/2}]^2}{[1-(1-a)^{1/2}]^2}$$

This formula is essentially the same as the one used by Taylor.

To find the actual value of the energy at an antinode and a node we must take account of the repeated reflection from the two ends of the tube. We know that the amplitude after reflection from the closed end is in the ratio $(1-a)^{1/2}$ to the incident amplitude. Suppose in the same way that we have an absorption coefficient b, *due to re-radiation*, for the open end. Then we have the following amplitudes:

Original beam, passing into tube from outside:	1
After reflection from closed end:	$(1-a)^{1/2}$
" " " open " :	$(1-a)^{1/2}$ $(1-b)^{1/2}$
" " " closed " :	$(1-a)$ $(1-b)^{1/2}$
" " " open " :	$(1-a)$ $(1-b)$
. . . . .	. . . . .

The total amplitude of all the waves travelling in the same direction as the original beam is then:

$$1+(1-a)^{1/2}(1-b)^{1/2}+(1-a)(1-b)+\cdots$$

and for waves travelling in the opposite direction:

$$(1-a)^{1/2}[1+(1-a)^{1/2}(1-b)^{1/2}+(1-a)(1-b)+\cdots]$$

We may add all the amplitudes, because the tube is tuned in resonance with the sound wave, and therefore all the waves are in the same phase. Summing the geometric series, we obtain $1/1-(1-a)^{1/2}\,(1-b)^{1/2}$ = amplitude of wave travelling in the same direction as the original beam, and $(1-a)^{1/2}/1-(1-a)^{1/2}\,(1-b)^{1/2}$ = amplitude of wave travelling in the opposite direction to the original beam. Then the amplitude at an antinode is equal to:

$$\frac{1+(1-a)^{1/2}}{1-(1-a)^{1/2}(1-b)^{1/2}}$$

and the energy at the same point, Ea, is equal to:

$$E_a=\left[\frac{1+(1-a)^{1/2}}{1-(1-a)^{1/2}(1-b)^{1/2}}\right]^2.$$

at the closed end of the tube is non-absorbing, a will be zero, and the energy If an antinode, E_0, will then be:

$$E_0=\left[\frac{2}{1-(1-b)^{1/2}}\right]^2$$

and the ratio of the energy at an antinode, when the end is absorbent to the value when the end is non-absorbing is

$$\frac{E_a}{E_0}=\left[\frac{[1-(1-a)^{1/2}][1-(1-b)^{1/2}]}{2[1-(1-a)^{1/2}(1-b)^{1/2}]}\right]^2.$$

E_a and E_0 are the quantities measured, and b is a constant for all measurements with the same pitch. If we, therefore, can find the value of b, it will be possible to calculate the absorbing coefficient a for the material under test.

Therefore, before using the tube we must calibrate it. In this case, the calibration is made in such a way that for several materials, where the absorption coefficients are known, the ratio E_a/E_0 is determined, and from all these an average value of b is calculated.

Apparatus

A tone of uniform intensity was produced by an organ pipe connected with a distant blower and a pneumatic tank. Pipes for different pitches, from C_1 (64 vibrations per second) up to C_6 (2069 vibrations per second) were tested, and the quality studied by means of a phonodeik. The pipes between C_1 and C_3 had overtones. If these pipes had been used, it would have been necessary to have a tone screen or a filter as described by Taylor. In the following measurements only two pipes were used, one near C_3 (295 vibrations per second), and one near C_5 (915 vibrations per second). These had no appreciable overtones. The calculations have been worked out only for the lower pitch, but several measurements have been made for the higher one, and, with the sound measuring apparatus used, it will be possible to test for still higher pitches. For the lower pitch the sound intensity had to be reduced to a suitable value by placing the pipe in a wooden box covered with several layers of thick felt. For the higher pitch the pipe was placed at a distance of about 1 m in front of the open end of the resonance tube.

The cross section of the resonance tube was a square, 7.5 by 7.5 cm. The length of the tube was 70.0 cm, it thus being possible to tune to resonance for the pitches 275 and 715 without moving the closed end of the tube a long distance. The tube was placed horizontally on a table. The bottom and the two sides consisted of 1/4 inch thick glass strips. The top was of wood, 2 cm thick; the inner surface carefully polished, and all joints were made tight by using putty or felt strips. The bottom and one side were covered outside the glass panels with 2 cm thick wood. The end of the tube fitted quite snugly, and could slide inside the tube for tuning.

For measuring the sound intensity, a Rayleigh disk, placed in the center of the tube itself was used. The disk was of mica, 1 cm in diameter, suspended on a very thin quartz fiber, about 2.5 cm long. The quartz fiber was fastened to a thin piece of brass that could slide along the wooden top of the tube. By means of a thin steel wire it was possible to move the disc from one end of the tube to the other, and the position of the disc could be read on a scale. A small mirror, about 1 mm^2, was fastened on the disk in such a way that when there was no sound, the mirror faced the open glass side of the tube. A light beam was reflected from the mirror to a scale. As the disc is initially at 45° and tends to set itself at right angles to the direction of the sound beam, this will produce a deflection on the scale. This deflection is approximately proportional to the sound intensity. The distance between the mirror and the scale was 45 cm, and the scale was 20 cm long. The arrangement is shown in Fig. 1.

The measurements were made in a very small room where the walls and the ceiling were covered with felt to diminish the reflection; but it was neces-

sary to have a partition also between the sound source and the place where the observer was working, because without it a small movement of the observer would change the standing wave system in the room, and therefore also the sound intensity in front of the resonance tube. In this case a screen of two layers of 1/2 inch thick felt was used, fitting tightly to the floor, walls and the ceiling. The tube was placed through a hole in the screen with the open end flush with the inner surface of the screen. To diminish disturbances from air currents, the open end of the tube was covered with very thin cheese-cloth when accurate measurements were to be made. The

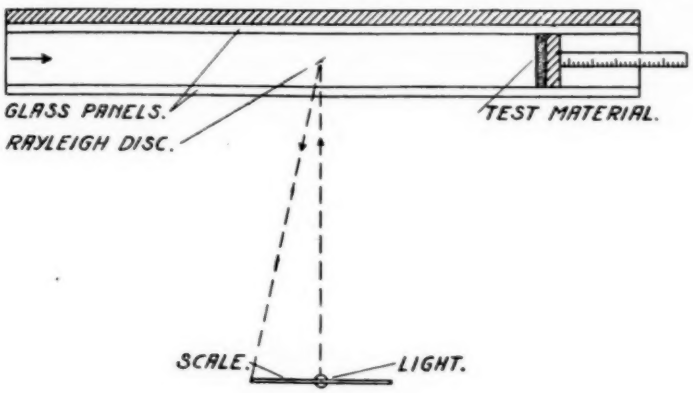

Fig. 1.

reflection from this end was increased about 10 percent on account of the presence of the cheese-cloth, but no harmful effects resulted. The curves show how satisfactorily steady the apparatus was, as thus arranged.

Experimental Results

The first measurements were made to determine whether there was measurable absorption inside the tube itself. Using the higher pitch, 915 vibrations per second, a measurement of the sound intensity was made from one end of the tube to the other. There were four antinodes in this length, and the maximum values were determined at these. These values decreased about 1.5 percent in passing from the one nearest the open end to the one farthest in. The effect of this upon the measurements would not be serious, and the error might be avoided by arranging to compare antinodes at the same position in the pipe, since the absorption is proportional to the sound intensity.

Absorption measurements were made for the lower pitch, 295 vibrations per second. Seven different materials with known coefficients were used. These coefficients had been determined by the reverberation method by Mr. Clifford M. Swan, at the Jefferson Physical Laboratory and are here published with his kind permission. As non-absorbing material, a plate of brass 2mm thick was used. The specimens of the materials under investigation were of the same size as the inside of the tube, 7.5 by 7.5 cm. Each measurement was made over a node and an antinode so as to determine the

wave-length. The value of the energy at a node was measured as well as possible, and from this the absorption coefficient was determined by Tay-

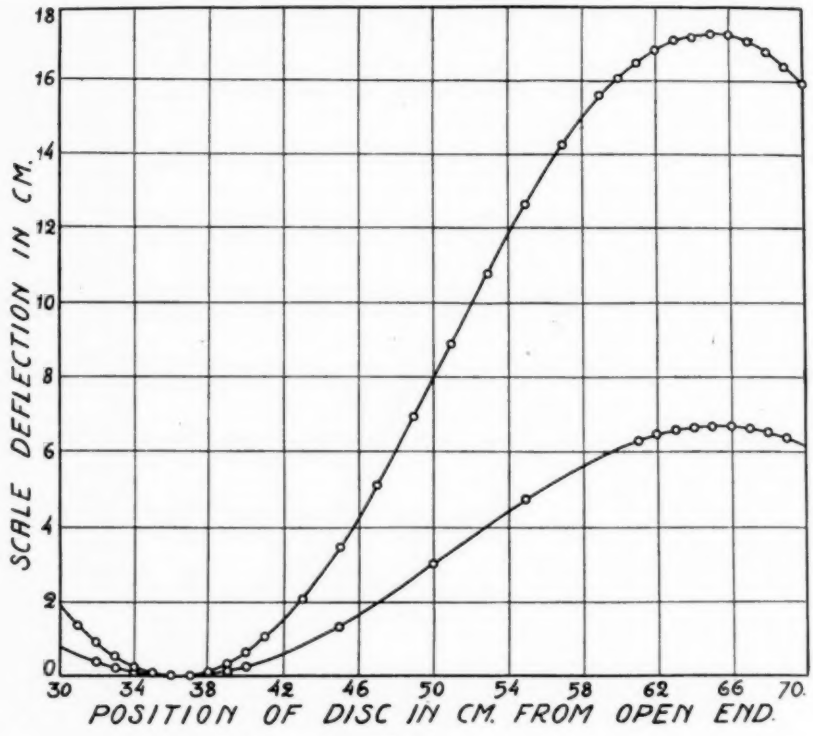

Fig. 2.

lor's method for comparison. With an accuracy of reading of about 0.2 mm, the possible error in these measurements by Taylor's method may rise to 30 percent. Fig. 2 shows a set of measurements from a node to an antinode

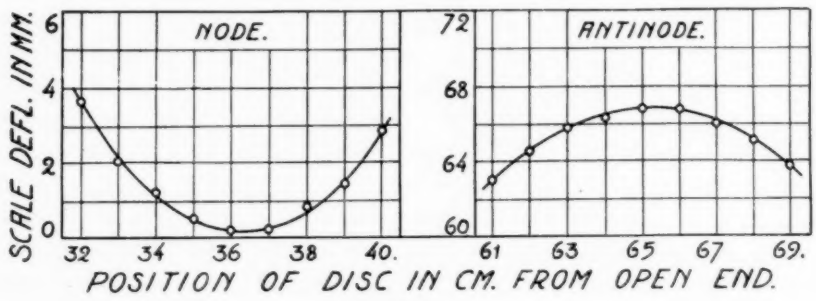

Fig. 3

for an absorbing and a non-absorbing material. Fig. 3 shows the minimum and maximum values in the case of the absorbing surface on a larger scale.

The measurement of an absorbing material was usually made between two measurements of the non-absorbing material and the average taken,

so as to avoid possible effects due to variations in the intensity of the source. The smoothness of the curves shows, however, that on the average the source was very steady.

The results of these measurements are given in the following table.

TABLE I

Absorption coefficients at pitch 295.

Material	E_a/E_0	Taylor's method		Sabine's method		Our method
		a	*b*	*a*	*b*	*a*
Commercial Celotex, 7/16" Not perforated.	0.364	0.21	0.31	0.16	0.23	0.17
Acoustical Celotex, 7/8" Perforated side exposed.	0.153	0.22	0.15	0.34	0.24	0.34
J. M. Asbestos Akoustikos Felt, 1/2" thick	0.403	0.16	0.27	0.25	(0.41)	0.15
Two layers J. M. Asbestos Akoustikos, 1/2" thick	0.109	0.35	0.18	0.45	0.25	0.43
J. M. Akoutikos Felt, 1" thick. (Older type)	0.455	0.15	0.28	0.23	(0.44)	0.13
Akoustolith, 1" thick. Tile	0.417	0.15	0.26	0.15	0.26	0.15
Rumford Tile, 1" thick.	0.272	0.19	0.21	0.22	0.24	0.22
Average value: $b =$			0.24		0.24	

In the first column we have the ratio E_a/E_0, where E_a is the maximum value of the energy in an antinode for an absorbing material and E_0 the same

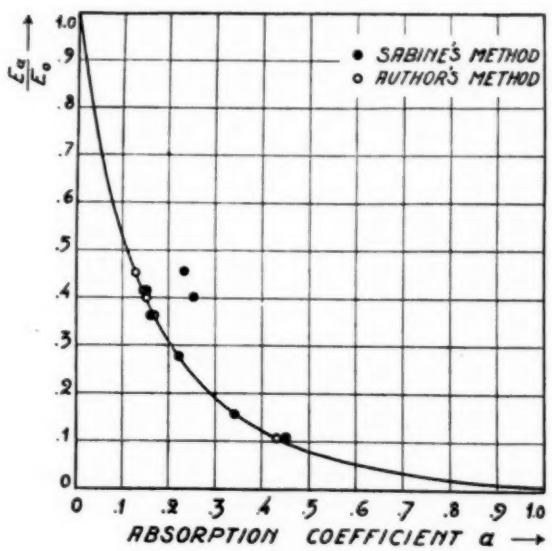

Fig. 4.

value for the non-absorbing material. In the next two columns the rough value of a calculated by Taylor's formula is given, and the value of b calculated from E_a/E_0 and a. The mean value of b is a little less than 0.24. In

the third and fourth columns we have the value of a determined by the reverberation method, here called Sabine's method, and the value of b calculated from this. In the last column we have the values of a, obtained by using the value 0.24 for b for the pitch 295 vibrations per second. The average value chosen for b is the same by both Taylor's and Sabine's method, provided we exclude two values, 0.41 and 0.44, which is done not only because the other values of b are so concordant, but because there may have been resonance phenomena due to vibrations of the felt itself in the measurements by the reverberation method.

Fig. 4 is plotted with the values of a taken from Table I for different materials as abscissae against E_a/E_0 as ordinates. Except for the two values just mentioned, these absorption coefficients from our method agree with the values obtained by the reverberation method.

It would seem from these results that the method is valuable for its convenience and is reasonably accurate for architectural purposes, at least through the range of absorption coefficients here indicated. For measurements on hard materials, the influence of the absorption in the tube and of the "non-absorbing" end may have to be taken into account, but they appear to be negligible for the materials tested.

I wish to express my thanks and indebtedness to Professor F. A. Saunders and Professor J. C. Slater for their interest and help in this work, and to Mr. C. M. Swan for the use of his valuable experimental results.

JEFFERSON PHYSICAL LABORATORY,
August, 1927.

THE PROPAGATION CHARACTERISTICS OF SOUND TUBES AND ACOUSTIC FILTERS

By W. P. Mason

Abstract

The process of measuring the propagation characteristics of uniform sound tubes and acoustic filters is complicated by the reflections which may occur at the ends of these structures. The present paper applies some theoretical results on the effect of reflections, obtained in a previous paper,[1] to the measurement of the propagation characteristics of tubes and acoustic filters. In making these measurements the device to be measured is inserted in an acoustic transmission system, and the resulting changes in the magnitude and phase of the transmitted wave are measured. The actual observations are made in electrical circuits connected with the terminals of the acoustic system by loud speakers. The impedance of the acoustic system at the point of insertion is made an acoustic resistance. For measurements on straight tubes, the acoustic resistances used are of such a value as to prevent any appreciable reflections from the ends of the tubes, and as a result, the propagation characteristics of an infinite tube are obtained. The results of the measurements on straight tubes indicate that the Helmholtz-Kirchoff law is valid, while the results of measurements on acoustic filters are in good agreement with the theoretical results obtained previously.

I. Introduction

THE transmission of sound waves in straight tubes has received considerable attention from physicists. On the theoretical side, a number of workers—notably Helmholtz and Kirchhoff,—have determined the effect of viscosity and heat conduction dissipation on the propagation of a wave in a tube of infinite length. They have shown that the vector ratios of the pressures or linear velocities at any two points of an infinite tube can be expressed as the napierian base e raised to the power αl, where l is the distance between the two points, and α is a complex number depending on the condition considered.

Attempts to check experimentally the Helmholtz-Kirchhoff law on the propagation of a sound wave in an infinitely long tube are complicated by the fact that in practice we must measure the transmission in a tube of finite length and hence one in which reflection of the wave motion occurs at the ends. A neglect of these considerations has led many observers to conclude that the Helmholtz-Kirchhoff law was not valid.

The Helmholtz-Kirchhoff law has two measurable quantities to check, the attenuation constant of the tube, and the velocity of propagation of sound in the tube. A number of measurements of the sound velocity[2,3] have

[1] W. P. Mason, "A Study of the Regular Combination of Acoustic Elements with Applications to Recurrent Acoustic Filters, Tapered Acoustic Filters, and Horns," Bell System Tech. Journal, April, 1927.

[2] The derivation of the Helmholtz-Kirchoff law and the attempts to check this formula are described by I. B. Crandall, "Theory of Vibrating Systems and Sound," D. Van Nostrand, 1926, p. 229–241.

been made, but apparently no measurements of the sound attenuation have been made in the range in which the formula should hold.[4] The early measurements did not check the Helmholtz-Kirchhoff law, but the later measurements indicate that the form of this equation is correct. E. H. Stevens[3] finds a variation of velocity with frequency greater than that given by theory, while E. Grüneisen and E. Merkel,[3] find values less than that given by theory.

The laws of reflection and the methods for taking account of them in the electric line—which is the analogue of an acoustic tube—have been well understood since Heaviside's work on the propagation of electric waves. Heaviside found it necessary to introduce another parameter besides the propagation constant—which is the analogue of the exponent of the e in the Helmholtz-Kirchhoff law—namely, the characteristic impedance of the line which may be defined as the ratio of the electromotive force to the current at the input of an infinitely long line. With these parameters he could express the relations between the current at any point in the line and the applied electromotive force for any boundary conditions at the ends of the line.

The Heaviside impedance method was first applied to the study of acoustics by Webster.[5] In his paper Webster introduces the characteristic impedance of a dissipationless tube. In a previous paper,[1] the writer has extended this method to take account of dissipation as well. The present paper applies these theoretical results to eliminate the effect of reflections in a finite tube, and measurements have been made which show that the Helmholtz-Kirchhoff law is entirely valid for propagation of sound waves in a smooth tube.

In the theoretical paper,[1] the combination of straight tubes to form acoustic filters, was considered. The use of the formulas taking account of the wave motion removes the assumption introduced by Stewart,[6] in his theory of acoustic filters, that no wave motion need be considered in the elements. These wave formulas take account of dissipation and in addition the effects of the terminating conditions have been investigated. An expression was obtained for the insertion factor, giving the absolute values of the ratios of pressures or volume velocities in the termination of an acoustic system with the filter in, to these quantities with the filter out. Hence this factor represents the effect of inserting the filter in a given acoustic system. The combination of filters whose conducting tube areas increase in some regular manner was also investigated, and it was shown that in addition to the filtering action, a transformer action takes place. Horns are the limiting cases of tapered acoustic filters, and their equations can be derived from those of tapered acoustic filters.

[3] E. H. Stevens, Ann. d. Physik **7**, 285 (1902)
E. Grüneisen and E. Merkel, Ann. d. Physik **66**, 344 (1921).

[4] L. F. G. Simmon and F. C. Johansen, Phil. Mag. **50**, 53 (Sept. 1925) give measurements at very low frequencies.

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To obtain an experimental check of the equations for acoustic filters, the same measuring circuit used to measure the straight tubes was employed, and a good agreement with theory was found.

II. Method of Measurement

The method employed here for measuring the transmission characteristics of acoustic devices is an adaptation of the ordinary electrical method for measuring insertion factors and insertion phase angle differences. The method consists primarily in transmitting energy, in electric or acoustic form, simultaneously over two parallel branches. One branch contains the structure under investigation, while the other contains an adjustable comparison circuit. The current reaching the termination of both can be compared both in magnitude and phase, by adjustments in the comparison branch and in the terminating circuit.

The knowledge ordinarily required about all electrical networks is what change will these networks produce when inserted in a given electrical

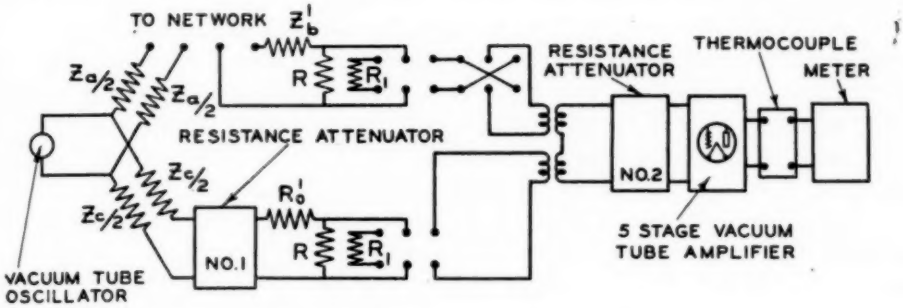

Fig. 1. Diagram of electric transmission measuring circuit.

system. That is, we need to know the ratio of the current in the termination of the system when the network is inserted to the current in the termination when the network is not in circuit. The absolute value of this ratio is called the insertion factor, while the difference in phase angle between the two currents is called the insertion phase angle difference.

The circuit employed for measuring these quantities is shown on Fig. 1. It consists in a source of sinusoidal voltage, here a vacuum tube oscillator, connected to two parallel branches, which in turn are connected to a terminating circuit by means of which the outputs from the two parallel branches can be compared.

The upper branch contains an input electrical impedance Z_a, and an output impedance Z_b. The terminating impedance Z_b is made up of an impedance Z_b' and a small resistance R. Wires from both sides of this resistance go to a double-pole double-throw switch, which on one side is connected to a resistance R_1, and on the other side to a reversing switch. From the reversing switch, wires go to one side of a three-winding transformer, with two equal input windings.

The lower branch contains an impedance Z_c in series with a resistance attenuator, which in turn is terminated in a resistance R_0. This resistance is made up to two parts, a resistance R_0' and a small resistance R. Wires from this resistance go to a double-pole double-throw switch and then to the other side of the transformer. The output of the transformer is connected to a second resistance attenuator, whose termination is connected to a vacuum tube amplifier and a thermocouple.

To measure the insertion factor and phase angle due to the unknown circuit, the impedance Z_c plus R_0 is set equal to Z_a plus Z_b. The resistance attenuators employed are combinations of resistances which have the property that when they are terminated in the resistance R_0, the impedance at the input terminals of the attenuator is always R_0. By turning the dials of the attenuator, various known ratios of output to input current can be obtained. Hence the current into the lower branch will have the value $e/(Z_a+Z_b)$. If the unknown network is not inserted in the upper branch and the impedances Z_a and Z_b are connected in series, the current in upper and lower branches will be identical both in phase and magnitude. The current in the output of the upper branch with the network inserted will obviously be the current which exists when the network is inserted between the impedances Z_a and Z_b and a source of e.m.f. e is placed in series with Z_a. Hence the ratio of the current in the impedance Z_c to the current in the impedance Z_b is the ratio of the current in Z_b with the network out of circuit to the current in Z_b with the network in the circuit.

To measure this ratio, the voltage in the upper branch across the small resistance R is impressed upon the succeeding circuit and by adjusting the gain of the amplifier a convenient reading is obtained on the meter connected to the thermocouple. Then throwing the upper branch switch to the resistance R_1, which has the same value of impedance as the circuit on the opposite side of the switch, and throwing the voltage across the resistance R of the lower branch through the succeeding circuit, a second reading is obtained. The resistance attenuator No. 1 is then adjusted, until a reading equal to the first is obtained. Hence the voltages across R for both branches are the same, and therefore the output currents of the two branches are equal. The value of the insertion factor can then be read from the resistance attenuator. The square of the insertion factor gives the insertion power ratio, that is, the ratio of the powers in the termination of the system when the network is in the system and out of the system. In all curves given, ten times the logarithm to the base 10 of the power insertion factor has been plotted so that the results are shown in the standard unit of attenuation, TU.

The method for measuring the phase angle is to compare the absolute values of the vector sum and vector difference of the currents from the two branches. This will determine the value of the angle, except that it will not be known whether it is in the upper or lower quadrants. By starting with a sufficiently low frequency whose phase angle is known, its location can readily be determined. To obtain the vector sum, both double-pole double-throw switches are thrown on the amplifier side, and a reading is obtained

which corresponds to the vector sum of the two equal currents, since an equality balance had previously been obtained. Throwing over the reversing switch, a reading corresponding to the vector difference of the two currents is obtained. By setting the resistance attenuator for no attenuation for the smaller of these two readings and varying it until an equal reading for the vector sum and vector difference is obtained, the ratio of the vector sum to the vector difference can be measured. The phase angle Θ and this ratio r are related by the formula

$$\cos \Theta = (r^2-1)/(r^2+1)$$

In applying this method for acoustic measurements, use is made of the fact that insertion factors and insertion phase angle differences, are respectively multiplicative and additive. That is, the insertion factor for a complete network, between the impedances Z_a and Z_b, is equal to the product of the insertion factor for a portion of the network, measured between the impedances Z_a and Z_b, and the insertion factor for the remainder of the network, measured between the impedances at the insertion junction looking toward and away from the source. Hence, conversely, the insertion factor of the portion of the network inserted last, measured between the impedances at the insertion junction, is equal to the ratio of the insertion factor of the total network to that of the first portion of the network, both measured between Z_a and Z_b. A similar result holds for the insertion phase angle differences except that these are additive rather than multiplicative.

To adapt this circuit for acoustic measurements the complete network was so constructed that the energy entering it was converted to acoustic form, traversed an acoustic path, was reconverted and emerged as electric energy. For this purpose two #555 Western Electric loud speaker units were utilized. A point in the acoustic path was taken as the junction at which the portion of the network, here the acoustic device under investigation, was inserted. The measurements gave the insertion effects of the device between the acoustic impedances of the path at the point of insertion. One problem then was to provide the proper acoustic impedances at this point of insertion. This has been accomplished by means of some acoustic resistances, which will be described below. The acoustic system used for these measurements consisted of a loud speaker unit, which was connected to an acoustic resistance, this in turn being connected to an exponential horn. The device to be measured was then inserted, and the same three units in opposite order were used to terminate the device and connect back to the electrical circuit.

The measuring process consisted in measuring the insertion factor and phase angle with the acoustic device in circuit; then taking the acoustic device out, that is, connecting the horns directly together, and measuring the insertion factor and phase angle again. In the same manner as in the electrical case, the ratio of the two measurements represents the insertion factor, while the difference between the phase angles represents the insertion phase angle difference, both measured between acoustic impedances looking in each direction at the insertion junction.

In order to determine what these impedances should be in the ideal case, and how much departure from the ideal may be permitted in practice, we must examine the relations between the propagation constant and the insertion ratio as a function of these impedances.

III. Determination of the Reflection Effects for Straight Tubes and Acoustic Filters

In measuring the reduction of volume velocity or the phase change due to any acoustic structure, we have always a given input and a given output boundary condition to satisfy. The knowledge of the acoustic structure generally required is what change will the structure cause when it is inserted in a given acoustic system. We define the volume velocity insertion factor of a given structure in a given system as the ratio of the volume velocity in the termination of the system when the structure is in the system to the volume velocity when the structure is out of the system. A similar factor can be defined for the pressure, but in symmetrical devices such as we are considering, the same insertion factor holds for both quantities.

To obtain this factor for a straight tube, use is made of the equations derived in the preceding paper.[1]

$$\begin{aligned} p &= p_1 \cosh \alpha L - (V_1 Z_L/S) \sinh \alpha L \\ V &= V_1 \cosh \alpha L - (p_1 S/Z_L) \sinh \alpha L \end{aligned} \tag{1}$$

where p is the excess pressure at the distance L from the beginning of the tube, p_1 the initial excess pressure at the beginning of the tube, S the cross sectional area of the tube, V the volume velocity at the distance L from the beginning of the tube, V_1 the volume velocity at the beginning of the tube, α the propagation constant and Z_L the specific characteristic impedance of the tube, *i.e.* the vector ratio per sq. cm of the pressure to the volume velocity for an infinite tube. α and Z_L for the frequencies of interest here are given by the formulas

$$\alpha = a + ib = \left[\frac{P\gamma'\omega^{1/2}}{2CS(2\rho)^{1/2}} + \frac{i\omega}{C} \left\{ 1 + \frac{P\gamma'}{2S(2\omega\rho)^{1/2}} \right\} \right] \tag{2}$$

$$Z_L = R + iX = (P_0\gamma\rho)^{1/2} \left[1 + \frac{P\gamma'}{2S(2\omega\rho)^{1/2}} - i\frac{P\gamma'}{2S(2\omega\rho)^{1/2}} \right] \tag{3}$$

where P is the perimeter of the tube, ρ the density of the medium, $\omega = 2\pi$ times the frequency, f, P_0 the average atmospheric pressure, γ the ratio of the specific heats of the medium, $C = (P_0\gamma/\rho)^{1/2}$ the velocity of sound in a dissipationless medium, $\gamma' = \mu^{1/2}[1 + (5/2)^{1/2}(\gamma^{1/2} - \gamma^{-1/2})]$, μ the coefficient of viscosity of the medium.

As shown in standard books, e^{-aL} is the ratio of the volume velocities, or pressures, at points of a tube of infinite length which are a distance L apart. bL, the phase constant, represents the phase rotation (in radians) between these two points. The velocity of propagation in a tube is C' where

$$C'=\frac{\omega}{b}=C\left\{1-\frac{P\gamma'}{2S(2\omega\rho)^{1/2}}\right\} \tag{4}$$

Assume now that the tube is terminated in an impedance Z_B/S, while at the input a source of simple harmonic pressure p_0, is placed whose internal impedance is Z_A/S. Then substituting in equation (1), the values

$$p/V=Z_B/S \text{ and } p_1=p_0-V_1Z_A/S$$

we obtain for V in terms of p_0, and the system parameters

$$V=\frac{p_0S}{Z_A+Z_B}\times\left[\frac{Z_A+Z_B}{2Z_B}\times\frac{2Z_L}{Z_L+Z_A}\times\frac{2Z_B}{Z_L+Z_B}\times e^{-\alpha L}\times\left\{\frac{1}{1-e^{-2\alpha L}\dfrac{(Z_L-Z_A)}{(Z_L+Z_A)}\dfrac{(Z_L-Z_B)}{(Z_L+Z_B)}}\right\}\right] \tag{5}$$

Now the volume velocity in the termination of the acoustic system if the tube were not present is obviously $p_0S/(Z_A+Z_B)$. Hence the ratio of the volume velocities of the system with the tube in and with the tube out will be the part of equation (5) in brackets. It can be shown that this factor will result for any structure which can be represented by a characteristic impedance and a propagation constant if these quantities are substituted respectively for Z_L and αL.

In measuring straight tubes, in order to check the Helmholtz-Kirchhoff law, we are interested in measuring the term $e^{-\alpha L}$. Hence, all factors except this must be eliminated or else corrected for. We notice that if $Z_A=Z_L$ or $Z_B=Z_L$, then the expression reduces to $e^{-\alpha L}$, and hence the insertion factor reduces to the propagation factor. Now the characteristic impedance of a tube, given by equation (3) is very nearly a pure resistance, it having in addition a small amount of negative reactance, which in general is less than two or three percent of the resistance for the frequencies of interest. Hence, if Z_A or Z_B are made pure resistances equal in value to Z_L, all terms but $e^{-\alpha L}$ are eliminated. Since it is difficult to make Z_A or Z_B exactly equal to Z_L the most accurate results will be obtained by letting $Z_A=Z_B$ and making them both as near Z_L as possible. So, if Z_A does not differ from Z_L by more than twenty percent in resistance, and if its reactance is not more than twenty percent of the absolute value of Z_L, the error caused by the first and third terms will not be more than 5 percent in power ratio or more than 0.1 radians in phase angle. This is about the accuracy of measurement of the power ratio, but somewhat less than the accuracy that can be obtained for the phase angle, which is about 0.02 radians. Hence if the measuring circuit is such that it gives the ratio of the volume velocities or pressures in the termination of an acoustic system with the tube in and out, and if impedance terminations are obtained which do not differ by more than 20 percent from Z_L, a system is obtained which will measure $e^{-\alpha L}$ accurately.

IV. Method for Obtaining an Acoustic Resistance

Equations (1), (2) and (3) show one method for obtaining an acoustic resistance, namely by using a long tube. The impedance of an infinitely long tube is Z_L. The impedance of a finite tube terminated in an impedance Z_1 is by equation (1), substituting $p = VZ_d/S$ and solving for $p_1/V_1 = Z_1/S$

$$\frac{Z_1}{S} = \frac{Z_L}{S}\left[\frac{(Z_d/S)\cosh \alpha L + (Z_L/S)\sinh \alpha L}{(Z_L/S)\cosh \alpha L + (Z_d/S)\sinh \alpha L}\right] \tag{6}$$

The impedances Z_d for which Z_1 will show the greatest variation from Z_L are zero and infinity. For these values, Z_1 is respectively

$$Z_L \tanh \alpha L \text{ and } Z_L \coth \alpha L \tag{7}$$

If the attenuation constant aL, of the propagation constant αL is made quite large, Z_1 will not depart far from Z_L. If for example the value of aL in equation (2) is 1.5, then the resistance component cannot vary by more than 10 percent from that of Z_L, and the reactance component will not be more than 10 percent of the resistance component. Hence if a long tube is put on each end of the acoustic device to be measured, a good termination is obtained, which satisfies the above requirements. The length of tube required, however, would be quite great. For example for the largest size tube measured below, the length of tube required for each end would be 34 meters if we wish to measure down to 200 cycles.

This length of tube is rather long for ordinary use, and hence some work has been done on methods for decreasing this length. One method for accomplishing this result is to build up the end termination out of smaller tubes, the sum of whose inside area equals that of the device we wish to terminate. With the smallest hexagonal tubes available, it was found that the length required on each end would be reduced to 6 meters in this way without causing the characteristic impedance to deviate by more than seven percent from the characteristic impedance of a long tube. This length being still rather long, two other methods were devised for reducing the tube length.

The first method employed was to use half of the tubes closed and half open. Since the tubes are all in parallel in the electrical sense, the total impedance of an open tube and a closed tube will be

$$\frac{Z}{S} = \frac{(Z_L/S_1)\tanh \alpha_L)(Z_L/S_1)\coth \alpha_L)}{(Z_L/S_1)\tanh \alpha L + (Z_L/S_1)\coth \alpha L} = \frac{Z_L}{2S_1}\tanh 2\alpha L \tag{8}$$

where S_1 is the area of a single tube. Hence an open and closed tube in parallel are equivalent to an open ended tube of twice the area and twice the length of either. By employing combinations of open and closed tubes the length can be decreased to one-half its former value.

The second method employed is to combine tubes which have the same characteristic impedance, but whose lengths differ among themselves. Starting with the shortest, the length from tube to tube is increased by an

equal amount in each case. To show what sort of an impedance such a combination will give, equation (6) is written in a different form

$$\frac{Z_1}{S_1}=\frac{Z_L}{S_1}\left[\frac{1-\dfrac{(Z_L-Z_d)}{(Z_L+Z_d)}e^{-2\alpha L}}{1+\dfrac{(Z_L-Z_d)}{(Z_L+Z_d)}e^{-2\alpha L}}\right]=\frac{Z_L}{S_1}\left[\frac{1-Ke^{-2\alpha L}}{1+Ke^{-2\alpha L}}\right] \tag{9}$$

where K is the volume velocity reflection factor $(Z_L-Z_d)/(Z_L+Z_d)$.

The impedance Z/S of n of these tubes in parallel, when the tube lengths are increased by a given amount Δ, from tube to tube, is given by the expression

$$\frac{S}{Z}=\frac{S_1}{Z_L}\left[\frac{1+Ke^{-2\alpha L}}{1-Ke^{-2\alpha L}}+\frac{1+Ke^{-2\alpha(L+\Delta)}}{1-Ke^{-2\alpha(L+\Delta)}}+\cdots+\frac{1+Ke^{-2\alpha(L+(n-1)\Delta)}}{1-Ke^{-2\alpha(L+(n-1)\Delta)}}\right] \tag{10}$$

Expandingthe expression and summing up the series, we obtain the infinite series

$$\frac{S}{Z}=\frac{S_1}{Z_L}\left[n+2Ke^{-2\alpha L}\left\{\frac{1-e^{-2n\Delta\alpha}}{1-e^{-2\Delta\alpha}}\right\}+\cdots+2K^ie^{-2i\alpha L}\times\left\{\frac{1-e^{-2ni\Delta\alpha}}{1-e^{-2i\Delta\alpha}}\right\}+\cdots\right] \tag{11}$$

Now the value of $(1-e^{-2n\Delta\alpha})/(1-e^{-2\Delta\alpha})$, if no dissipation is assumed, is shown on Fig. 2, and is equivalent to the expression for the light from

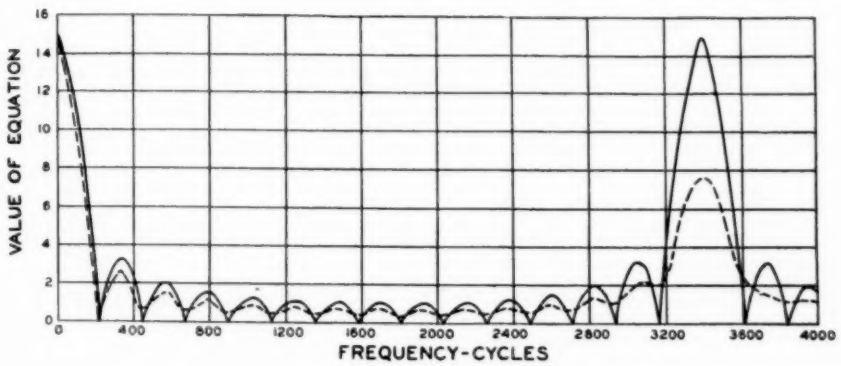

Fig. 2. Typical plot of equation $(1-e^{-2N\Delta\alpha})/(1-e^{2-\Delta\alpha})$. (Solid line gives non-dissipative case, dotted line shows effect of dissipation)

a diffraction grating between two successive images. It generally is around the value 1 except near the upper and lower end of the curve. The effect of dissipation is to smooth out this curve, as shown in Fig. 2, which gives the case actually used here. This expression is multiplied by $e^{-2\alpha L}$ which generally is a small number. For the case considered here it has the value

.25 at 1000 cycles. Hence above this frequency, all terms except the first two can be neglected, since they contain powers of $e^{-2\alpha L}$, and since the value of $(1-e^{-2ni\Delta\alpha})/(1-e^{-2i\Delta\alpha})$ is generally around 1. When the second term approaches the value 1, it will affect the absolute value of the impedance by less than the factor $(n-1)/n$ and hence if n is large, the total impedance will be nearly

$$Z/S=Z_L/nS_1$$

The lowest frequency for which this occurs will be when the length $2n\Delta$ is one wave-length.

Fig. 3, shows the acoustic resistance actually used for these measurements. It consists of 37 hexagonal brass tubes fitted together into a hexagonal form, leaving no space between the tubes. Thirty of these are grouped in pairs, one tube of each pair having an open end and the other tube a closed end. The lengths of these pairs vary from 38.1 cm to 73.6 cm in equal

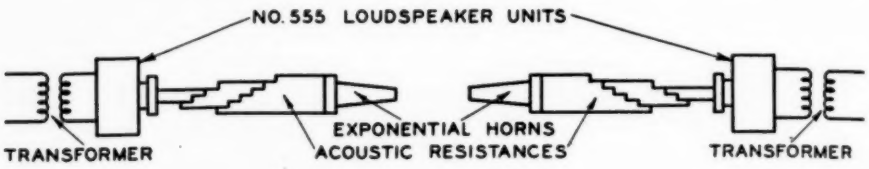

Fig. 3. Acoustic section of transmission measuring circuit.

steps. From wall to wall the diameter of these tubes is 0.32 cm. The seven tubes in the center are somewhat longer than the others, each of these being 78.8 cm, and are connected to the #555 loud speaker. They are used to conduct sound into the system, or to take off a small amount of sound at the receiving end. These tubes are only a small part of the total, and their length is such that no matter what their termination is, the impedance that they contribute to the total terminating impedance cannot vary by more than forty percent. As their area is a small fraction of the total, their effect on the terminating impedance is small.

The entire acoustic circuit is shown on Fig. 3. As we wish to measure several sizes of tubes, and it is inconvenient to use more than one size of acoustic resistance, some logarithmic horns were used to taper down from the acoustic resistance to the size of tube to be measured. It has been shown previously,[1] that the characteristic impedance per sq. cm of a logarithmic horn remains unchanged throughout its length and hence the horn acts as a transformer. Furthermore, if we are interested in frequencies which are large compared to its cut-off frequency, the characteristic impedance is nearly that of a straight tube. The horn used here was one having a cut-off frequency of 55 cycles. At frequencies above 400 cycles, the irregularities introduced by the horn were less than 10 percent. Corrections for the horn distortion have been made on the measurements of the two smallest tubes up to 400 cycles. All other measurements given are the insertion factor measurements as made using the above circuit.

V. Experimental Results

Measurements have been made of the attenuation constant of four tubes of different diameters. The phase constant of the smallest tube has also been measured. The radii of the tubes measured were 0.851 cm, 0.687 cm, 0.525 cm, and 0.370 cm, while the corresponding lengths were 622 cm, 488.5 cm,

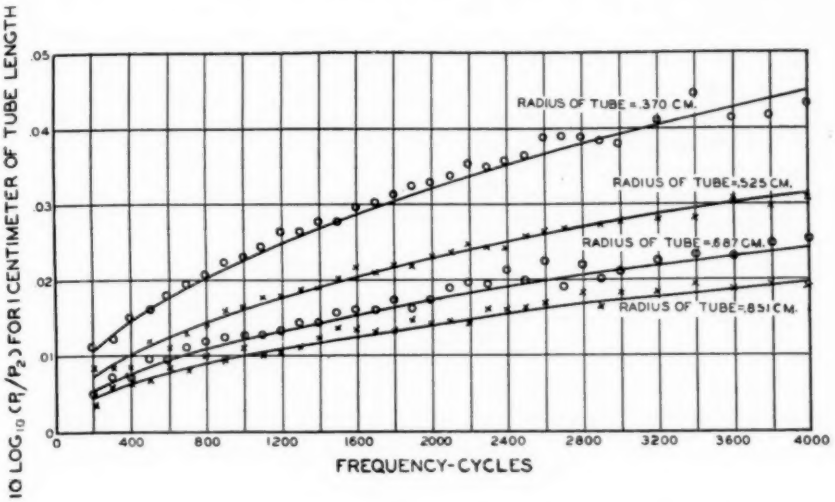

Fig. 4. Measurements of attenuation characteristics of four tubes.

426 cm and 763.4 cm. The thickness of the brass tube walls was about 1.02 mm. All measurements were made at room temperature, which averaged about 23.5°C. The measured values of the insertion power ratios are given by the points on Fig. 4. All values have been expressed per centimeter of tube length. The solid lines of this figure are a plot of the theoretical values

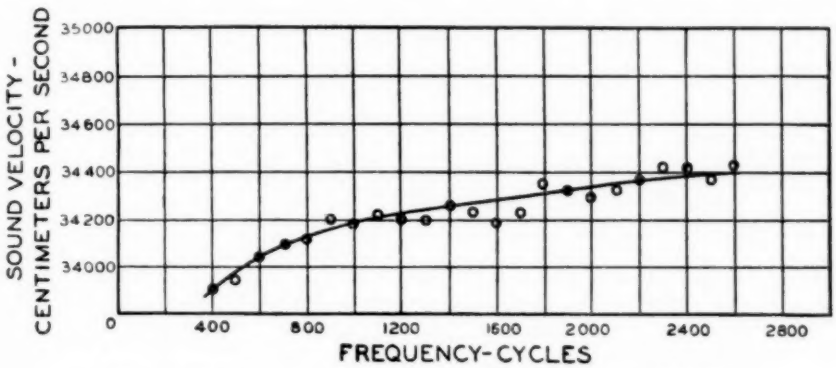

Fig. 5. Measurement of the velocity of sound in a small tube.

given by equation (2), assuming a value of μ of 1.86×10^{-4}. It is evident that the measured and theoretical values are in good agreement, and hence it appears that the Helmholtz-Kirchhoff law holds very well for the tubes measured, for frequencies from 200 to 4000 cycles.

A plot of the measured phase constant is shown on Fig. 5. What is plotted is ω/b, which is the velocity of propagation. By means of equation (4) and the known constants of the tube, we can calculate the theoretical value of the velocity for this tube. The result is shown by the full line of Fig. 5.

Measurements have been made of the insertion power ratio of two acoustic filters. The filter used, shown in Fig. 6, consists of a main conducting

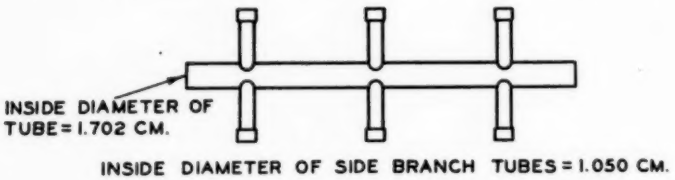

Fig. 6. A typical acoustic filter.

tube and two side branches at each junction point. By putting on or taking off caps, the side branches could be either closed or opened on the end. The first filter, a low-pass type, was obtained by putting all the caps on the side branches. The second, a high-pass type, was obtained by removing all of the caps. Since the side branch is small compared with the main conducting tube, we take the end correction for the side branch to be 0.82 R.[7] With this

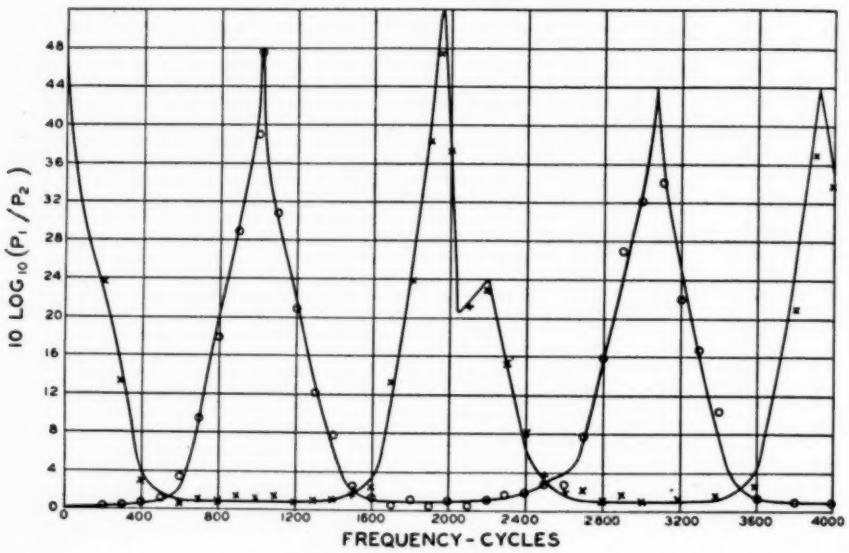

Fig. 7. Measurements of the insertion losses of two acoustic filters.

correction, the length of the side branch closed is 8.49 cm, and the length open is 8.79 cm. The distance between successive side branches is 16.7 cm. The total number of sections employed is three.

[7] Reference 1, page 263.

The measurements of these filters are shown by the points on Fig. 7. Calculated values of the insertion power ratio, making use of equations (25) and (31) of the preceding paper,[1] to give the filter parameters to be inserted in equation (5) of this paper, are given by the solid lines of Fig. 7. In making these calculations, the terminating impedances Z_A and Z_B have been taken as resistances whose values were $(P_0\gamma\rho)^{1/2}$ per sq. cm. The degree of agreement is shown by the figure.

VI. Discussion of Results

The results obtained for the attenuation measurements of straight tubes, which are little affected by temperature changes, indicate that the sound energy attenuation obeys closely the Helmholtz-Kirchhoff law. Since no means were available for preserving a constant temperature during the experiment, no great accuracy can be claimed for the deviation of velocity with frequency measurements. The results obtained agree with the Helmholtz-Kirchhoff law within the accuracy of measurement. The results obtained for the acoustic filter measurements agree well with the theoretical values and indicate that all assumptions made are valid.

The measuring method and circuit gives results accurate to about 5 percent in power ratio and about .02 radians in phase shift. In order to utilize the phase accuracy, it would be necessary to maintain a constant temperature and to have acoustic resistance terminations which do not vary by more than 5 percent from the characteristic impedances of the tubes. This last requirement can be met by eliminating the logarithmic horns, and by using acoustic resistances with longer tubes than were employed here.

In conclusion the writer wishes to express his thanks to Professors Wills and Webb of Columbia University for their interest in the investigation.

Bell Telephone Laboratories, Incorporated,
May 26, 1927.

BOOK REVIEWS

A Short History of Physics. H. BUCKLEY. Pp. 263. D. van Nostrand, New York, 1927, $3.00.

"This book is an attempt to give in simple and exact manner an historical account of the development of physical science from its earliest origins to the present day." In writing it the author has realized that "for the general reader, or for the specialist in one branch of science who is the general reader in another, the historical method is usually more interesting than . . . .the more formal and logical method . . . ." The book should prove of considerable value to this class of reader, for here is presented the subject matter and content of physics in a quickly accessible form, with no mathematics. The many quotations from original sources add to the value of the book. The method of treating the subject by separate topics will also doubtless be of advantage to this class of reader, although this has disadvantages when one tries to gain a comprehensive view of the entire field. The recent developments are not treated as fully as their importance would seem to justify. In a book bearing the date Jan. 25, 1927, one would expect to find at least the names of Compton, Born, and Schrödinger.

To the physicist who expects to gain deeper insight into the nature of physics the book will be a disappointment; it is too much in the nature of a mere chronicle of events, compiled by the author from outside. Some day a different sort of history will be written which will enable the reader to live himself back into the physics of the past. Such a history will be more concerned with the great ideas, with their origin, growth, and decline; it will portray the outstanding difficulties and problems which confronted each generation of physicists; it will try to give some impression of the personalities of the successful discoverers, and will show how at some periods certain qualities have been essential to success, and at others, others: it will not omit to show how experimental discovery has gone hand in hand with improvement in experimental technique, and will give some account of the development of technique; and finally, we may expect some discussion of the part which the development of physics has played in the evolution of civilization.

P. W. BRIDGMAN

The Structure of the Atom. E. N. DA C. ANDRADE. Pp. 750, 112 figs, 8 plates. Harcourt, Brace and Company, 1927. Price $10.00.

In entering its third edition this noted and note-worthy text has expanded tremendously, attaining 750 pages and approaching the dimensions of what in Germany would be called a "Handbuch."

About 160 pages are devoted to the phenomena from which the masses, the charges, the force-fields and the stability or instability of the atom-nuclei are deduced. Positive-ray analysis, Moseley's experiments, and the deflections of alpha-particles by atoms are described at length. Dr. Andrade justly gives more than the usual attention to Lenard's work upon scattering and retardation of electrons by matter, and to the discrimination between single, plural and multiple scattering; on the other hand, the deflection of very slow electrons by atoms is treated too briefly, and without mention of Minkowski and Sponer or of Davisson and Kunsman. Barkla's work upon the scattering of x-rays is described, and so are the deductions of Debye and Bragg concerning the arrangement of electrons about atom-nuclei in crystals, but not those of Duane and Havighurst. The treatment of radioactivity is full and thorough, in respect both of the phenomena and of the models proposed for nuclei. In considering the question whether the emisson of gamma-rays from an atom undergoing beta-ray transformation occurs before or after the beta-ray is emitted, the author seems to have reversed his opinion midway in the chapter! The description of the disintegration of atom-nuclei by the impacts of alpha-particles is the best I know.

The attack upon the theory of the extra-nuclear electrons, begun in Chapter IX after anticipatory allusions, is conducted mainly according to the methods of Bohr and the pertur-

bation-theory. The principle of adiabatic invariance is introduced almost at the start, and is well expounded; then comes the principle of correspondence, explained probably as clearly as this essentially vague "principle" can be explained. Stark effect and Zeeman effect for the hydrogen atom are deduced in full detail by Bohr's method, and the relativity-effect both by this and by Sommerfeld's method. It may be remarked in passing that the classical theory of Zeeman effect does not imply that all electrons yielding the p-component are vibrating parallel to the field, and that the adverse criticism of LoSurdo's method of producing the Stark effect is probably invalidated by Foster's successes. The spectra of atoms with more than one electron are analyzed in the way customary before the advent of the spinning electron, with detailed accounts of the work of Hartree and Fues upon the forcefield representing the effect of the inner electrons. Wien's experiments on canal-rays and others bearing upon the duration of stationary states are described; not, however, those of Webb or Eckart. Next comes an excellent chapter on excitation-potentials, including a long account of thermal excitation, Saha's equation, Fowler's and Milne's variants thereof, and some of the relevant astrophysical data; and containing also Einstein's derivation of Planck's equation, and an account of collisions of the second kind. The chapter on x-ray spectra is more of the conventional type, and exemplifies the confusion prevailing before the spinning electron resolved the paradoxes of "relativity" and "screening" doublets.

In the chapters entitled "Periodic Properties" and "The Static Atom Model" Dr. Andrade has assembled a remarkably great quantity of chemical data, thus providing himself with abundant material from which to show the powers and the limitations of various atom-models, and the defects of the Periodic Table itself; providing himself also with opportunity for a number of pungent and mostly well-deserved comments on recent theories. Especially to be noted are the detailed discussion of Abegg's rule; the analysis and illustrations of the word "valency"; the series of Grotrian diagrams displaying the variations in the values of corresponding terms from one to another member of the families of one-and two-valence-electron atoms; the description of Bohr's way of accounting for the "interpolated" groups of elements, such as the rare earths; the account of the hafnium-vs-celtium controversy; the work of Born and Landé upon the theory of heteropolar crystals, and the Rankine on the viscosities of gases. In the chapter "Magnetic properties" we find the conventional theories of diamagnetism and paramagnetism, the gyromagnetic effect, the Weiss-vs-Bohr-magneton battle, the paramagnetism of ions as function of their number of electrons, the Gerlack-Stern experiment and Whittaker's atom-model. This chapter is very fluent, and especially refreshing after the struggle with the preceding one, which is entitled "Multiplet Structure and Anomalous Zeeman Effect" and was written in cognizance of the work of Landé and Pauli upon Zeeman effect, the brilliant idea of Russel and Saunders on which Hund's work is based, and the first papers, of Hund himself. Not even Dr. Andrade could make this subject pleasant reading; but the mastering of the chapter will be valuable to anyone, however much the theories in this field may subsequently evolve.

Anyone who has attempted or even considered the writing of a book on atomic theory will realize what difficulties the author of "The Structure of the Atom" must have met: the hard choice between omitting important subjects or letting the book swell beyond reason—the unending stream of issues of the Zeitschrift and the Proceedings and the Review, each of which might contain some paper requiring the rewriting of a whole section—the fear lest on the day after the book has irrevocably gone to press, some tremendously important and subversive paper change the whole aspect of theoretical physics. Dr. Andrade has not been favoured by fortune; the spinning electron appeared just in time for a footnote, the matrix-mechanics for a few pages, the wave-mechanics for a sentence. Yet it becomes increasingly evident that not only the data of experiment, but the mathematical methods used in solving or interpreting the problems set by the data, usually survive the mutations of viewpoint and analogy which follow on one another's heels so rapidly in modern physics; and while several sections of this book are now superfluous and several require drastic revision, much the larger fraction may stand unchanged through edition after edition.

It remains to be said that the style of "The Structure of the Atom" is throughout distinctly above the level customary in books in physics; and in occasional pages Dr. Andrade attains a felicity of verbal expression unsurpassed by any who write on science today.

It would be interesting to know why a book which is sold for $7.30 in England is offered at $10 in this country.

KARL K. DARROW.

Optische Methoden der Chemie. FRITZ WEIGERT. Pp. 632, 341 figs. 16 tables and one colored table. Akademische Verlagsgesellschaft, Leipzig 1927.

The science of photochemistry has been greatly retarded by its unusual experimental difficulties. As one of the foremost contributors to the theoretical and experimental development of the subject, the author has been in a position to appreciate those obstacles and doubtless the present work had its inception in a desire to make their conquest easier. That his object has been attained, can not be questioned, but the book has been given a much broader scope by extending it to treat the principal points of contact between chemistry and optical methods, as is shown by the subject matter which is divided into fifteen chapters of the following titles: General Remarks on Optical Instruments and Their Use, Light Sources, Radiation Filters, Operations of Photography, Spectroscopy, Photometry, Spectral Photometry, Colorimetry and Nephelometry, Color Measurement, Energy Measurements, Photochemical Measurements, Microscopy and Ultramicroscopy, Determination of Refraction of Light, Analysis of Polarized Light, Investigation of Faint Light Phenomena, Luminescence. An Appendix contains tables of the principal lines of a number of elements, lines of the iron arc, tables for the method of ultraviolet spectral analysis, Newton colors for air and silver films and notes to the 16 tables.

On the hand, the work has the character of a detailed Handbook which would serve Optical Chemistry in the same way that the Ostwald-Luther-Drucker Handbook has served Physical Chemistry in general. On the other hand the book presents the broader outlines of each subject in its present state of theory and development without going into the details of the experimental results. The author shows a grasp of his subject, which comes only from close contact and long experience in its investigation. An innovation, which the author has had the courage to make, should be generally welcomed. Every writer feels the desire to include at the last moment references to the latest work, when it can no longer be done without disturbing the entire paging of a chapter or more. This, Weigert has accomplished by utilizing waste space on the last page of several chapters to introduce new material as an addition to one or more paragraphs in the interior of the chapter. Several such additions in a single page do not detract from its appearance and add much to the usefulness of the book.

S. C. LIND

Elementary Principles of Statistical Mechanics. J. WILLARD GIBBS. Pp. 195+XVI, Librairie Scientifique J. Hermann, Paris, 1926, price unbound $1.90.

French translation by F. Cosserat, revised and completed by J. Rossignol, with an introduction by M. Brillouin. Gibb's great book has finally been translated into French. As Brillouin states in his introduction, the translation had been started at his instigation long ago, but, due to external difficulties, has been completed only after the death of Mr. Cosserat. A number of tests prove the translation to be carefully and accurately done. The translator has added some explanatory foot-notes without giving an elaborate comment to the text, a task which, while very difficult would, in the opinion of the reviewer, be extremely useful.

K. F. HERZFELD

Kinetic Theory of Gases. LEONARD B. LOEB. Pp. 555+XVI, 76 figs. McGraw-Hill, New York.

Until recently the kinetic theory of gases has not received the attention of text book authors, in English speaking countries, it deserved. Only Jeans' classical work has been available, but the rigorousness of its mathematical deductions puts it on too high a level for the average student of experimental physics or physical chemistry. Recently, a translation of a rather elementary French book, by E. Bloch, has appeared. We are fortunate that now, almost at the same time, two books are published filling the gap, one by Tolman, and the other by Loeb. The subject is so vast that the two overlap very slightly. Loeb's book should be understood also by students who are not very far advanced. It gives a very detailed and complete mathematical development of the results which should enable everybody, equipped

with the calculus necessary for any physicist, to follow it. Usually it precedes its mathematical derivations with a short statement of the physical side so that the reader may see what it is all about. Then, follows a very complete discussion of experimental results brought up to the latest date. Especially commendable is the large number of figures representing partly experimental results, but to a large extent being sketches for the theoretical deductions. This should greatly help the understanding. The content of the book is as follows:

It starts with the usual introduction to the theory of perfect gases, introduces then the free path and continues with a very thorough discussion of Maxwell's distribution law. Especially useful in these chapters is the discussion of related phenomena as the free paths of electrons, electron emission from hot bodies, and the influence of the Doppler effect on the width of spectrum lines. The next chapter deals with Van der Waal's equation. Then follows one chapter on viscosity, heat conduction and diffusion. Next, the behavior of very rarified gases, especially the experiments of Knudsen, are treated in a very thorough manner. This part includes surface phenomena like adsorption.

Then, leaving the gas theory proper, we find a treatment of the Brownian movement, and of the specific heat of gases and solids with a short introduction to the quantum theory. The next part gives a very useful exposition of the kinetic theory of dielectric and magnetic substances according to the theories of Langevin and Debye. The last chapter, which was the most interesting to the reviewer, deals with the kinetic theory of ionic mobility in gases to which the author of this book has so largely contributed. I do not know of any other modern exposition of this subject in English.

Besides the many praiseworthy qualities of the book, there are some minor features about which the reviewer has a different opinion. First of all, it seems that the author has sacrificed several times the precision of statement and the rigidity of the logical argument to an apparent smoothness of diction, which indeed will make the book more readable to the poorer students, but may cause difficulties to more independent thinkers. The second objection is that in the discussion of the Van der Waal's forces, the author follows Van der Waal's original but now antiquated assumptions of forces with a range large compared with molecular distances. He does not point out that for all we know now this is not at all true. Debye has shown that Van der Waal's result can as well be reached with the opposite assumption. Connected with this subject is the unfortunate fact that the author repeats on pages 159–160 an argument of W. McLewis, in which he deduces from Van der Waal's a/V^2 that the forces must be proportional to $1/r^4$. Debye has again shown that no such connection exists.

But the mentioning of these minor slips, the avoidance of which is almost impossible in a first attempt, should not detract from our recommendation of the book, but only help to improve the next edition, which, I am sure, will be soon necessary.

K. F. HERTZFELD

Weather Observations and Aids to Forecasting. DONALD W. HORNER. Pp. 64, 12 figs. George Allen and Unwin, Ltd. London, 1927.

The author of this work expects it to be used as a college textbook, and assures us that "great care has been taken to verify every fact." It takes about an hour to read it—an hour of wasted time, except for the fun of correcting about as many errors as there are pages.

One amusing page assures us that for 37 kilometers above the troposphere (itself 10 kilometers deep, or more) there is no change of temperature with elevation; and, further, that above the isothermal layer is the stratosphere (two names for the same region) extending roughly to 24 miles above the earth's surface!

Another burst of humor appears in the novel explanation of the London fog, caused, the author says, by the cold, damp air rising from the river and mixing with the warmer and drier air of the town.

In discussing meteorological apparatus, only one reference is made to an American type—and that is wholly wrong.

Such books as this—and they are innumerable—goad one almost, if not quite, to the point of wishing that there might be some sort of a "pure food" law applicable to publishers. Anyhow, a drastic solution of some kind is urgently needed.

W. J. HUMPHREYS

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY

MINUTES OF THE NASHVILLE MEETING

DECEMBER 28, 29, 30, 1927.

The twenty-ninth Annual Meeting (the 148th regular meeting) of the American Physical Society was held at the Ward-Belmont School, Nashville, Tennessee, on Wednesday, Thursday, and Friday, December 28, 29, and 30. The presiding officer was Professor Karl T. Compton, President of the Society. The attendance was about one-hundred and fifty.

The annual joint session with Section B was held on Wednesday afternoon. Professor Karl T. Compton presided in the absence of Professor A. H. Compton, Chairman of Section B. The retiring Vice-President, Professor William Duane, opened the joint meeting with an address entitled "The General Radiation." This was followed by an address by Dr. C. J. Davisson on "Diffraction of Electrons by a Crystal of Nickel," with discussion by Professor J. H. Van Vleck.

On Thursday afternoon Professor Karl T. Compton delivered the presidential address, his subject being, "Recent Studies of the Electrical Discharges in Gases."

On Thursday evening, December 29, there was a dinner for members of the Society and of Section B and their friends at the Ward-Belmont School, attended by one-hundred and sixteen persons.

Annual Business Meeting.—The regular annual business meeting of the American Physical Society was held on Friday morning, December 30, at eleven o'clock. A canvass of the ballots for officers resulted in elections for the year 1928 as follows:

President;	K. T. Compton
Vice-President;	Henry G. Gale
Secretary;	Harold W. Webb
Treasurer;	George B. Pegram
Members of the Council,	L. J. Briggs
Four-year term;	H. L. Bronson
Members of the Board of	R. S. Mulliken
Editors of the Physical	H. D. Smyth
Review, Three-year term;	I. S. Bowen

The Secretary reported that during the year there had been 138 elections to membership. The deaths of 10 members had been reported during the year, 34 had resigned and 23 had been dropped. The membership of the

Society on December 30, 1927 was as follows; Members, 1440; Fellows, 473; Honorary Members, 7; Total Membership, 1920. The numbers are approximate because they include elections and transfers at the November and December meetings. In the year there has been a net increase of 75 members, a net decrease of one fellow, and the loss of one honorary member.

The Treasurer presented his financial report for the year 1927. The Managing Editor presented the financial report for the PHYSICAL REVIEW for the year 1927. In his report of the condition of the Review he stated that from a study of the rate of change of membership and of the rate of increase in the size of the Review it was estimated that the Review would show a profit until about the year 1931, when the cost of publishing will be about equal to the receipts.

Changes in the type of program of the meetings of the Society were discussed at length. It was brought out that the present policy of limiting the meetings to ten minute papers has resulted in a loss of interest. On motion of Professor William Duane, it was resolved that it was the sense of the meeting that one session at each meeting should be devoted to invited papers summarizing various fields of research.

Meeting of the Council.—At the Meeting of the Council held on December 28, 1927, five persons were transferred from Membership to Fellowship, and twenty-four were elected to Membership. *Transferred from Membership to Fellowship:* Samuel K. Allison, Robert B. Brode, J. B. Green, Fabian M. Kannenstine, Samuel C. Lind. *Elected to Membership:* A. J. Ahearn, Alexander J. Allen, Lewis Balamuth, Niel F. Beardsley, Clyde F. Benner, William M. Ewing, Basim Faris, Otto Glasser, Edwin K. Jaycox, Harry A. Kirkpatrick, Charles R. Larkin, Evan J. Lewis, Fleming G. Moore, R. J. Munce, Jr., J. R. Oppenheimer, C. H. Prescott, Jr., J. Alingh Prins, Hubert H. Race, R. William Shaw, Kenneth B. Stoddard, Ernst K. G. Stuckelberg, Harold R. Voorhees, Hsioh Ren Wei, Jerrold Zacharios.

The regular program of the American Physical Society consisted of 55 papers, Numbers 6, 13, 14, 20, 29, 33, 34, 35, 38, 40, 41, 51, and 55 being read by title. The abstracts of these papers are given in the following pages. An Author Index will be found at the end.

HAROLD W. WEBB, *Secretary.*

ABSTRACTS

1. A simple color analyzer. T. D. PHILLIPS, Marietta College.—Using a differential color mixer and a set of filters a rapid method of color analysis of pigments has been devised. The results closely approximate those obtained by more elaborate means.

2. The use of the grid-glow tube as an electrostatic voltmeter. T. R. WILKINS and F. B. FRIEND, University of Rochester.—The neon grid-glow tube has been used for the measurement of potentials applied between the grid and anode: the anode and cathode being shunted by a variable capacity. The period of discharge can be varied through wide limits by altering the plate potential, grid resistance (of order of 10 megohms) and shunt capacity. By suitable adjustment, great sensitiveness in the range 0-1 volt grid potential can be secured making the tube a valuable instrument for the measurement of small potentials where the quantity is very small. Under certain conditions, the period of discharge is directly proportional

to the capacity shunted between the anode and cathode. A method is thus given for the comparison of capacities.

3. An electrical method of harmonic analysis. S. LEROY BROWN, University of Texas.—The plan of this method of harmonic analysis of a periodic electromotive force is to exaggerate the measured effect of each higher frequency component approximately proportional to the cube of the order of the harmonic. The electromotive force to be analyzed furnishes current into an input circuit, consisting of a fixed, known capacity and a fixed, known inductance in series, when the values of the capacity and inductance have been so chosen that the input circuit tunes to a frequency higher than the frequency of the highest order harmonic that is being measured. Another inductance is loosely coupled with the inductance of the input circuit and a variable condenser across this second inductance permits the second circuit to be tuned to the fundamental or to one of the several harmonics of the current that is flowing in the input circuit. A vacuum tube voltmeter is connected across the tuning condenser and the relative amplitude of harmonic to fundamental is calculated from the peak values of voltmeter readings, calculated values of the input impedance, measured values of the resistance of the tuned circuit at the respective frequencies and the order of the harmonic.

4. Some experiments concerning the nature of the sensitive point in the Geiger counter. L. F. CURTISS, Bureau of Standards.—A study has been made of a number of different treatments for the points used in the Geiger electrical counter. Following the suggestion put forward by Geiger (Zeits. f. Phys. **27,** 7 (1924)) that the action of the counter might be readily understood if the point in its sensitive condition is coated with a film of high electrical resistance, points have been prepared by coating them with materials which might be expected to give such a film. Although in most cases some beneficial effect was noted, few were very satisfactory as regards permanence. On treating steel points with phosphoric acid, and some similar substances, it has been found possible to produce points which are very sensitive and reliable. The method has also been found to work repeatedly without failing, a great advantage over the flame treatment. Geiger's view of the nature of the action of the counter is more nearly in accord with the results of these experiments than the view expressed by Kutzner (Zeits. f. Phys. **23,** 117 (1924)).

5. Completion of 75 cm reflecting telescope and photoelectric photometer. ROBERT H. BAKER, University of Illinois.—The new apparatus will be used for studies of minute variations in the quantity and quality of starlight. Disks of borosilicate crown glass for the telescope mirrors were made by the Spencer Lens Company and figured by John E. Mellish. All mechanical and electrical work was done by the J. B. Hayes Machine Company. The ratio of the 75 cm primary mirror, aperture to focal length, has the unusual value 1 to $2\frac{1}{2}$. The effective ratio at the Cassegrainian focus is 1 to 12. A quartz reflecting prism in the cell box may be rotated so as to divert the beam of starlight upon either of two photo-electric cells. The rates of increase of positive potential of the cells are measured by two string electrometers which hang in gimbals from the cell box. Sliding electrical contacts are avoided in this arrangement. Kunz cells are used, one caesium, the other sodium or potassium. Preliminary observations suggest that the apparatus will serve the purpose for which it was designed.

6. A triode amplifier for small direct currents. ALEXANDER MARCUS, The College of the City of New York.—Most of the methods of using thermionic vacuum tubes for the purpose of amplifying small direct currents rely either on the Wheatstone network or on the potentiometer principle in separating the normal value of anode current from the small change superimposed upon this value by the much smaller grid current which is being amplified. These balance methods are found to be highly unstable owing to the large disturbances produced by slight changes in the various battery voltages. It is found that the simplest method of maintaining stable working conditions whenever the current amplification does not exceed several hundred is to employ only an "A" battery with the triode, the filament voltage being adjusted just enough below normal to reduce the anode current to zero. Lowering of the filament voltage has the effect of minimizing deterioration of the filament while the current amplification is not

seriously reduced thereby. The life of the tube is also prolonged indefinitely and the calibration of the tube-galvanometer combination remains permanent. This type of "thermionic galvanometer" is being employed to measure ionization currents, photo-electric currents, and piezo-electric currents of magnitudes considerably below the range of the galvanometer when used without the triode.

7. The use of the cathode-ray oscillograph in the study of resonance phenomena in piezo-electric crystals. K. S. VAN DYKE, Wesleyan University.—The piezo-electric resonator in series with a known resistance (A) forms one side of a bridge; the other side consists of a known impedance in series with a second known resistance (B). The deflecting systems of the cathode-ray oscillograph are connected so that one indicates the potential across A and the other that across B. When a source of alternating potential whose frequency is independent of any reaction from the resonator is applied to the bridge, the oscillograph indicates by a Lissajous figure the relative magnitudes and phases of the currents in the two arms. The impedance of the resonator at frequencies near resonance may be computed from measurements on the figure for those frequencies, and the constants of the electric network equivalent of the resonator (Phys. Rev. **25**, 895 (1925)) obtained therefrom. The figure also readily indicates whether the resonator is responding to the fundamental or to some harmonic in the source. The work of determining the natural vibration frequencies of quartz resonators and their equivalent networks is in progress.

8. An improved form of cathode ray oscillograph. R. H. GEORGE, Purdue University.—This oscillograph was designed for maximum flexibility, in order to be readily adaptable to a wide variety of work. It is constructed almost entirely of metal, and arranged for inserting photographic plates and films in the vacuum to obtain permanent records of transient phenomena. By employing interchangeable cathode parts the accelerating potential of the beam can be varied from less than 100 volts to thousands of volts, depending on the deflectional and photographic sensitivites required. The deflecting plates are adjustable, and as many as three pairs can be used at one time, making possible three simultaneous deflections by electrostatic fields. Magnetic deflecting coils may also be employed when desirable. Methods are described for making leak proof joints, for interchangeable parts, lead-in connections and for driving a film drum from outside the vacuum. Requirements for emulsions sensitive to electron bombardment are discussed, and methods described for making sensitive emulsions, and for sensitizing the ordinary photographic plates.

9. Electrical resistance and magnetic permeability of iron wire at radio frequencies. G. R. WAIT, Carnegie Institution, F. G. BRICKWEDDE and E. L. HALL, Bureau of Standards.—(A) Mitiaev observed (Zeits. f. Phys. 1926) that the high frequency resistance of iron wire underwent a critical change at about 100 meters wave-length. This he considered a confirmation of the results of Wwedensky and Theodortschik on the critical change in permeability of iron. In view of contrary results on permeability by Wait (Phys. Rev. **29**, 566 (1927)) it was decided to investigate the high frequency resistance. The resistances of wires intermediate in size between those used by Mitiaev were measured by the resistance-variation method as described in Bureau of Standards Circular 74. The investigation was carried out between 79 and 120 meters. No critical change within the observable accuracy was detected. (B) The difference in results between those of Wwedensky and Theodortschik and those of Wait, on the permeability of iron in alternating fields might be due to a difference in the kind of iron. The variation in permeability of a sample in which the phenomena had been observed by Wwedensky and Theodortschik was determined with the same apparatus and under the same conditions as by Wait. Smaller fields and various methods of binding the sample were also tried. In no case was a critical variation observed.

10. The overshooting of the temperature of a tungsten filament. LESTER I. BOCKSTAHLER, Northwestern University.—Using a double strip oscillograph, simultaneous photographic records were made of the heating current in a straight filament tungsten lamp and the thermionic current emitted by the central portion of the filament. The records showed that, upon

closing the circuit, the expected momentary overshooting of the heating current was followed by a marked overshooting of the thermionic current. Since the thermionic current indicated the temperature of the filament, there was an overshooting of the power consumption when the current was turned on the cold filament. As a check, one strip of the oscillograph was connected to record the heating current and the other to record the potential drop across the central portion of the filament. The product of the corresponding ordinates of these records and an appropriate constant, obtained from voltmeter and ammeter readings, also showed an initial overshooting of power. The magnitude and duration of this initial surge depended on the final temperature and the size of the filament. The "end effects" of the filament were eliminated by the use of "potential leads" and guard rings. To minimize the inductance and the potential drop in the line, a large capacity storage battery, joined to the lamp with short heavy copper leads, served as a source of current.

11. Specific resistance and purity of sodium electrolyzed through soda-glass. J. RUD NIELSEN, University of Oklahoma.—(1) The specific resistance was measured by observing the resistance of a U-shaped capillary tube filled first with mercury and afterwards with sodium. Taking the specific resistance of mercury to be $94073\times10^{-9}\times(1+0.0008892t+0.000000994t^2)$ the following results were obtained. For solid sodium between 30° and 90°C.

$$4661\times10^{-9}\times(1+0.00484t);$$

for liquid sodium below 160°C.

$$9828\times10^{-9}\times(1+0.00354(t-100)+0.00000039(t-100)^2).$$

(2) The sodium was obtained as described by Burt (J.O.S.A. & R.S.I., **2,** 87 (1925)). A spectroscopic analysis, by a method which is a modification of that developed by Gooch and Hart (Am. J. Sci. **42,** 448 (1891)), showed that the sodium contained 0.08 percent potassium. No other impurities were detected.

12. The resolving power of an octahedral crystal for x-rays. CARLETON C. MURDOCK, Cornell University.—An investigation of the relation between the size of octahedral crystals of the cubic system and the width of the lines of their x-ray power spectrogram shows that the half intensity width B of a line is given by an equation of the same form as that developed by Scherrer for the case of cubic crystals: $B=K\lambda/D\cos(\theta/2)$, where λ is the wave-length of the x-rays used, θ the angle of diffraction and D the length of the crystal measured between opposite corners. K is a numerical coefficient approximately equal to 1.6. Its value is a function of the indices of the spectral line. Several experimenters have used Scherrer's equation to compute the size of colloidal particles of materials such as gold and platinum, which ordinarily crystallize in the octahedral form. If we compute the particle volume from their data considering the crystals as octahedra the result is about twenty percent less than that obtained by assuming the crystals to be cubes.

13. The molecular and crystal structure of ethane. JARED KIRTLAND MORSE, University of Chicago.—The results of this investigation indicate that while the bond in the ethane molecule between the carbon atoms is the generally accepted two-electron bond that between the hydrogen nuclei and their respective carbon atoms consists of a single electron. The following interatomic distances are found C–C 1.26A and C–H 1.54A. The carbon atoms appear to be cubical with a radius R of 0.77A as observed in the diamond lattice. In the crystal structure of ethane these molecules are arranged in a close-packed hexagonal array. The lattice constants of this structure referred to orthorhombic axes are found to be geometrically related to the radius R of the carbon atom. $a_0=4R(6)^{1/2}=7.54$A, $b_0=4R(2)^{1/2}=4.36$A and $c_0=32R/3=8.21$A. The carbon nuclei are found to have the positions 0 0 0, 1/12 7/12 5/8, 1/6 1/2 1/2, 5/12 7/12 1/8, 1/2 1/2 0, 7/12 1/12 5/8, 2/3 0 1/2, 11/12 1/12 1/8, and the hydrogen nuclei the positions 0 1/3 15/16, 1/12 1/4 3/16, 1/6 5/6 15/16, 1/4 3/4 3/16, 1/3 1/3 5/16, 5/12 1/4 3/16, 1/2 5/6 15/16, 7/12 3/4 3/16, 2/3 1/3 15/16, 3/4 1/4 3/16, 5/6 1/6 15/16, 11/12 3/4 3/16, 0 1/3 7/16, 1/12 1/4 11/16, 1/6 5/6 7/16, 1/4 3/4 11/16, 1/3 1/3 7/16, 5/12 1/4 11/16, 1/2 5/6 7/16, 7/12 3/4 11/16, 3/3 1/3 7/16, 3/4 1/4 11/16, 5/6 1/6 7/16, 11/12 3/4 11/16. The diffraction effects computed from the above structure

agree within the limits of experimental error with the measurements of Mark and Pohland (Z. Krist. **62**, 103–109 (1925)). The 004 plane gives an abnormal reflection. It should be absent when the diffracting centers are considered to be concentrated at the centers of the carbon atoms but it is present as observed when the structure factor is computed from the electronic positions.

14. The lattice constants and the space groups of $BaCO_3$ and $SrCO_3$. THOMAS A. WILSON, General Electric Co.—Precision x-ray photographs were taken of Merck's $BaCO_3$ and $SrCO_3$ by the powder method with Mo K radiation using NaCl as a calibrating substance. In both substances the fundamental lattice is the simple orthorhombic Γ_0, and the unit cell contains 4 chemical molecules. The unit cell of $BaCO_3$ has the dimensions: $a_0=5.252\pm.001$A, $b_0=8.828\pm.002$A, $c_0=6.544\pm.001$A. The calculated density is $4.291\pm.004$. The axial ratios (0.5949:1:0.7413) and the density (4.28–4.37) given by Groth are in agreement with the data. The unit cell of $SrCO_3$ has the dimensions: $a_0=5.118\pm.003$A, $b_0=8.404\pm.005$A, $c_0=6.082\pm.004$A, and the calculated density is $3.722\pm.006$. The dimensions agree with the axial ratios (0.6090:1:0.7237) given by Groth, but the density (3.680–3.716) of Groth is somewhat lower than that given by the x-ray. The space group of $BaCO_3$ is $2Di-16(X=a)$ agreeing with that found by Wyckoff (Am. Jour. of Sci. **9**, 145 (1925)) for aragonite. That of $SrCO_3$ is probably $2Di-16(X=a)$ but because of the fogging of the films it was impossible to establish this with the same certainty as that of $BaCO_3$.

15. On the x-ray analysis of chromium-nickel alloys. F. C. BLAKE, JAMES O. LORD, W. C. PHEBUS and A. E. FOCKE, Ohio State University.—It has previously been reported that chromium distorts the nickel lattice up to 64 percent chromium but it was not possible until now to determine the correct status of the alloy for higher percents of chromium, although it was reported that a body-centered chromium nickel lattice separated out for alloys rich in chromium. By proper etching and x-ray analysis of the undissolved material it is shown that a third phase which is rhombohedral, with many lines, is present. It is this rhombohedral lattice together with the body-centered lattice that is present for alloys containing from 65 to 85 percent chromium. Microphotographs taken of the samples confirm the presence of three phases.

16. Indices of refraction of platinum for x-rays of long wave-length. ELMER DERSHEM, University of California.—Using a total reflection method with apparatus placed in a vacuum spectrograph the indices of refraction of platinum have been measured over the wave-length range 1.279 to 7.01 Angstrom units, yielding values of $1-\mu$ of 27.3×10^{-6} to 663×10^{-6}. This region extends to lower frequencies than those of the absorption limits of the K, L, and M series. The results show that the simplified form (neglecting absorption) of the Drude-Lorentz dispersion formula can not be used although in the parts of the region farthest removed from an absorption limit it leads to results of the same order of magnitude as those found experimentally.

17. X-ray diffraction in liquid normal paraffins. G. W. STEWART, University of Iowa.—X-ray diffraction was studied in liquid pentane, hexane, octane, nonane, decane, dodecane, tetradecane and pentadecane. There was one diffraction peak only, instead of two as found by Stewart, Morrow and Skinner with the primary alcohols and certain isomers and with normal fatty acids. This peak was located at the same angle as with the other liquids referred to and possessing normal carbon chains. This angle, interpreted by Bragg's law, indicates a lateral separation of 4.6A. The absence of the second peak, indicating a longitudinal arrangement is accounted for by a consideration of the molecular structure and the longitudinal forces. It is significant that in six of the nine paraffins, the diffraction intensity does not decrease as the diffraction angle approaches zero. Assuming that the carbon atom occupies a length in the chain of 1.3A, the hydrogen atom, 1A, and that the volume of the molecule is the square of the lateral spacing by the length, the computed values of densities of the seven normal paraffins are correct to within less than 4 percent, or a mean of 2 percent. The other two paraffins are evidently isomers instead of normal and are not included. Two additional faint peaks are found

with pentadecane and tetradecane. The corresponding spacings are 2.1A and 1.23A. The nearness of these to the repetitive values of 2.0A and 1.26A which are found in the diamond is suggestive.

18. Fine structure in the K series of molybdenum. BERGEN DAVIS and HARRIS PURKS, Columbia University.—We have already shown that by proper arrangement of crystals the resolving power of the double x-ray spectrometer may be much increased. (Proc. Nat. Acad. Sci. **13,** June, 1927.) With both crystals at first order reflection the Kβ doublet was completely resolved. It has since been found that by placing crystals for higher orders of reflection, the resolving power is increased. If $d\lambda$ is the wave-length interval to be observed $2nd\lambda = 2d \cos \theta_n d\theta_n$. The angular separation $d\theta_n$ increases with order. In addition the resolving power is further increased by the fact that the rocking curves become narrower at higher order. Measurements here given were made at second order on both crystals. Fine structures were observed as follows all on long wave-length side of parent line: β_1' at .17 X-U from β_1; α_1' at .085 X-U from α_1 and α_2'at .096 X-U from α_2. The α_2' line was diffuse indicating that it might be further resolved into components. Measurement attempted at third order on α_1 gave same $d\lambda$ as at second order.

19. The K x-ray absorption edge of iron. H. R. VOORHEES and GEO. A. LINDSAY, University of Michigan.—The K x-ray absorption edge of iron was photographed, using as reflecting crystals several different iron compounds—pyrite, hematite, arsenopyrite, epidote, and lepidomelane. The iron in these crystals gave the characteristic K absorption edge without the use of any other absorbing screen. The absorption was also obtained by screens of iron compounds, and by a thin screen of electrolytic iron. When screens were employed, a sylvan crystal was the reflector. A complicated fine structure of the edge was observed, extending over a range of more than 200 volts. The spectral range of fine structure due to the stopping of the ejected electron in different virtual orbits would be much smaller than that obtained here, and such an hypothesis is quite inadequate to explain the present observations, especially in the case of the uncombined element. It is, therefore, supposed that at least part of the fine structure is due to the simultaneous ejection of two or more electrons from the atom.

20. A diagram of the properties of crystals. JAKOB KUNZ, University of Illinois.—In his lectures on problems of atomic dynamics, delivered at the Massachusetts Institute of Technology, M. Born has given a diagram (due to Heckmann) of the crystalline properties omitting however, the magnetic properties. A new diagram has been made which includes the magnetic properties as well as their relations to temperature and to mechanical and electrical forces.

21. Thermoluminescence excited by x-rays. Further experiments upon synthetically prepared materials. FRANCES G. WICK and MABEL K. SLATTERY, Vassar College.—Many materials originally inactive are made thermoluminescent by exposure to x-rays. $CaSO_4$ containing a small amount of manganese in solid solution shows this effect strongly and has been previously studied by the authors. The present report gives a continuation of this work upon sulphates of cadmium, calcium, sodium and zinc containing a small amount of manganese. Exposure to x-rays produces two kinds of change in the material. One of these results in a thermoluminescence which comes up quickly upon heating and lasts for a very short time while the other is shown by a luminescence which comes up more slowly and lasts longer. If the material is allowed to stand at room temperature after exposure the first effect disappears in a few hours while the second may last for months. Both of the effects may be preserved indefinitely by keeping the specimen in liquid air after exposure. The decay of thermoluminescence was studied using different temperatures of observation, different temperatures of exposure and different voltages on the x-ray tube. Exposure to ultra-violet light of a definite frequency was found to kill the effect produced by exposure to x-rays. The results obtained are compared with effects of exposure to cathode rays as described by Weidemann and Schmidt.

22. Further studies in the effect of x-rays upon certain optical properties of liquids and glass. FRED ALLISON, Alabama Polytechnic Institute.—Magnetic and optical rotations induced in several liquids when exposed to x-rays have been observed by the author (Chicago

Meeting, 1927). In these liquids the induced optical rotation is left-handed, while the induced magnetic rotation is in the same direction as, and increases with the Faraday rotation. By varying the field strength the induced magnetic and optical rotations may be made to compensate, the former predominating in stronger and the latter in weaker fields. In sugar and tartaric acid solutions x-rays increase the right-handed rotation roughly in proportion to the concentration. Since distilled water traversed by x-rays shows a slight left-handed rotation, it is possible to find a concentration of the sugar or acid solution in which the rays induce no rotation. A left-handed rotation appears as the solution is further diluted and a right-handed one as its concentration is increased. X-rays are found to induce in glass in a magnetic field a rotation in opposition to the Faraday rotation. The above induced rotations as observed are all small, being of the order of a few minutes. They increase with the potential across the x-ray tube.

23. Positive ions reflected from a metallic surface. R. W. GURNEY, Princeton University, (Introduced by H. D. Smyth, Princeton University.)—The velocities and intensities of potassium ions scattered from a platinum surface have been measured by allowing the scattered ions to pass through the slits into the electric and magnetic fields of a positive ray box. The source was a Kunsman filament mounted on a ground glass joint so that the target could be bombarded from any angle. On varying the field in the positive ray box, and plotting intensities against the field-strength, a peak is obtained in the usual way, and from the position of this peak the velocity of the reflected particles is known. It was found that when the target was cold the position of the peak was almost independent of the velocity of the primary beam, the scattered ions never having more than a few volts energy when that of the incident beam was raised from 8 volts to 80 volts. But when the target was glowing (by means of a heating current) the scattered particles retained from 10% to 80% of their initial energy, their energy varying continuously with the angle of incidence and being greater for smaller glancing angles. On allowing the target to cool, the peak rapidly returned to its former position at a few volts, presumably due to a contamination of the surface by grease vapor from the ground glass joint.

24. Diffraction of electrons by a single layer of gas atoms adsorbed upon a nickel crystal. C. DAVISSON and L. H. GERMER, Bell Telephone Laboratories, Inc.—The first gas atoms to adhere to a clean $\{111\}$ surface of a nickel crystal give rise, under electron bombardment, to plane grating electron diffraction beams, which show that these first atoms arrange themselves in a structure similar to a $\{111\}$ layer of nickel atoms, but with twice the scale factor of the latter. These plane grating beams pass through broad maxima due to constructive interference with differential diffraction beams arising from two different classes of surface nickel atoms (Phys. Rev. **30**, 705 (1927)). There is some freedom in calculating from these data the separation of gas atoms from the plane of the surface nickel atoms; the gas atoms may lie above alternate second layer nickel atoms or above alternate third layer atoms, and for some of the maxima the order is uncertain. If the gas atoms are assumed to lie above alternate third layer nickel atoms and at about 3.A from the plane of the first layer atoms then the calculated occurrences of the diffraction maxima (6 in number) are in acceptable agreement with the six maxima which were observed (loc. cit.). This separation of 3.A is over twice the apparent separation of surface layers of nickel atoms (1.4A).

25. The relative activation of a nitrogen-hydrogen mixture by electrons and by K^+ ions in the formation of ammonia. C. H. KUNSMAN, Bureau of Chemistry and Soils, U. S. Department of Agriculture.—The activation chamber consisted of a Pyrex bulb containing a tungsten filament as the electron source, an iron-potassium coated strip as the K^+ ion source, and a fine platinum gauze cylinder as the collector. The (N_2+3H_2) mixture at pressures of 1 mm and less was introduced in the bulb immersed in liquid air and the rate of decrease in pressure or formation of NH_3 was shown for various conditions of the hot surfaces. Results show that without an applied potential the iron-potassium catalyst surface is very much more active in the clean-up than the tungsten, but that a large increase in the rate with tungsten takes place at electron speeds of 17 volts and over, while no appreciable increase is observed with K^+ ions from the catalyst surface up to 330 volts speed. These results are in agreement with other comparable properties of electrons and ions, such as ionization and secondary electron emission from surfaces.

26. On electrical fields near metallic surfaces. JOSEPH A. BECKER and DONALD W. MUELLER, Bell Telephone Laboratories, Inc.—If an electron must pass through surface fields in order to escape from the surface, a properly directed applied field, F, should partially neutralize the surface fields and hence increase the thermionic current i. A simple analysis shows that $d(\log_{10} i)/dF = (11600/2.3T) \times s$. T = surface temperature; s = distance from the surface at which the surface field equals F. For clean surfaces the observed current-voltage relation can be accounted for if the only force acting on the escaping electron is due to its image field. For composite surfaces such as thorium on tungsten another field, due to the adsorbed ions, is superposed on the image field. Close to the surface this "adsorption field" is very intense and helps electrons escape thus decreasing the work function; farther from the surface this field reverses sign, grows to a maximum value and then steadily decreases. This reverse field has appreciable values at surprisingly large values of s. Hence the log $i - F$ curve for composite surfaces is steeper than that for clean surfaces.

27. Secondary electron current as a function of crystal structure. H. E. FARNSWORTH, Brown University.—Several experimenters have attempted to correlate the breaks which appear in the secondary electron curve (secondary current as a function of primary energy) of a metal with soft x-ray and optical levels of the atoms composing the metal, but without much success. The results given here together with some previous ones show that the changes in slope of the secondary electron curve for copper in the region 0–40 volts are characteristic of the arrangement of the atoms at the metal surface, and not of the structure of the atoms themselves. The curve for a phosphor bronze target does not show the characteristics of the curve formerly obtained for copper. The curve for targets cut from a single crystal of copper is distinctly different from that previously obtained for a large number of targets taken from copper sheet.

28. A series of measurements of critical potentials of Hg vapor. J. C. MORRIS, JR., Princeton University.—A seven electrode tube was designed to determine the critical potentials of mercury by the various methods previously employed and to compare the efficiency of the different methods. By suitable connections the tube can be employed according to the Lenard method, inelastic impact method of Hertz and Franck, Franck and Einsporn method, Davis and Goucher method for distinguishing ionizing and radiating potentials, Hertz method for critical potentials by inelastic impacts, as well as the usual methods for determining ionizing potentials. The photo-electric methods have not yielded the resolution expected and several unexplained irregularities have developed. The radiating potentials have been resolved most successfully by the Hertz method. Using a molybdenum filament there was slight evidence of ionizing potentials above 10.4 volts but by employing a Wehnelt cathode burned at very low temperatures these were resolved to check the values previously reported by Lawrence. Taking the lowest ionizing potential as 10.4, the values found were 10.4, 10.65, 11.34 and 11.8. From the curve the relative probabilities of the different types of ionization can be determined.

29. An analysis of the fine structure of the D_3-line of helium. H. R. WEI, University of Chicago.—The D_3-line of helium λ5875 has been found to be a triplet under conditions suitable for true spectroscopic resolution. A new type of discharge tube which is free from absorption and Stark effect and can be cooled with liquid air at reduced pressure was used. The D_3-line was photographed in the higher orders of a 30-ft. Littrow with 8-inch and 10-inch gratings, and also with a 30-step echelon. Microphotometric traces of the photographs from both instruments show clearly the triplet structure of the D_3-line. An analysis of the traces gives the intensity ratio of 5:3:1 and the separation ratio of about 10:3:1 for the triplet. The results are in good agreement with the theoretical predictions of Heisenberg and the intensity measurements of Burger. A discharge tube similar to the one employed by Houston (Nat. Acad. Sci. Proc. **13,** 91 (1927)) was examined. The appearance of the D_3-line with this tube was found to be chiefly due to self-reversal.

30. Self-reversed lines in the spectrum of mercury. L. H. DAWSON and W. H. CREW, Naval Research Laboratory.—Spectrograms in the region λ6000 to λ1860 were made of a mercury arc in quartz operating at atmospheric pressure and excited by a condensed discharge.

Eleven arc lines and two spark lines were observed to be self-reversed. All of these arc lines, except λ2536, represent electron transitions originating on the 2^3P levels, which are the lowest energy levels of the excited Hg-atom. Furthermore, six of these lines start on the 2^3P_1 level, two on the 2^3P_0 level, and two on the 2^3P_2 level, indicating a predominant accumulation of electrons on the supposedly least stable orbit; the frequent collisions due to pressure possibly preventing the usual accumulation on the more stable orbits. By means of absorption, electrons appear to be raised to the 3^3D_1 level by two avenues of approach, to the 3^3D_2 level by one and to the 3^3D_3 level by none. Consistent with this is the observation that of three emission lines commencing on these levels, the most intense starts on the 3^3D_1 level, and the least intense on the 3^3D_3 level. The same holds for the 4^3D orbits. The arc when excited by 4000, 8000, and 16000 kilocycles at 5, 1, and 0.5 amperes respectively gave sharp atomic lines, and also molecular bands coincident with those usually observed in fluorescing mercury vapor.

31. Certain multiplets in the spectra of Cb III and Cb IV. H. E. WHITE and R. C. GIBBS. Cornell University.—Applying the irregular doublet law to the data already known for the triad of multiplets ${}^3D_{1,2,3}-{}^3P_{0,1,2}$, ${}^3D_{1,2,3}-{}^3D'_{1,2,3}$ and ${}^3D_{1,2,3}-{}^3F_{2,3,4}(ds-dp)$ in the two electron systems Sr I and Yt II, the corresponding multiplets for Zr III (unpublished zirconium data obtained from C. C. Kiess) and Cb IV have been identified. Similarly the triad of multiplets ${}^4F'_{2,3,4,5}-{}^4D'_{1,2,3,4}$, ${}^4F'_{2,3,4,5}-{}^4F_{2,3,4,5}$ and ${}^4F'_{2,3,4,5}-{}^4G'_{3,4,5,6}$ (d^2s-d^2p) in the three electron systems of Yt I, Zr II has been extended to Cb III, and the stronger lines in the ${}^4F'G'$, multiplet of Mo IV have been identified. In passing successively from element to element in both of these iso-electronic systems the shift in the frequency of the radiated lines for each of these multiplets is approximately constant. Assuming that $(\nu/R)^{1/2}$ varies according to the Moseley Law, and that $\Delta(\nu/R)^{1/2}$ is independent of atomic number, in accordance with the irregular doublet law, and using the observed radiated frequencies of each element, and the known term values of Sr I, the term values of each level have been computed.

32. The regular displacement of certain multiplets for elements in the second long period. R. C. GIBBS and H. E. WHITE, Cornell University.—The strongest lines and multiplets arising from the electron transition $4p$ to $4s$ in the presence of 0, 1, 2, 3 · · · 10, $3d$ electrons, for those elements in the first long period of the periodic table starting with K I, have been shown to follow a regular displacement on a frequency-atomic number diagram. A similar relation is also found to hold for the corresponding multiplets for elements in the second long period starting with Rb I. Here, however, the electron transition is from $5p$ to $5s$ in the presence of 0, 1, 2, 3, · · · 10, $4d$ electrons.

33. Characteristics of the neutral and of the singly and doubly ionized spectra of praseodymium, neodymium and samarium. ARTHUR S. KING, Mount Wilson Observatory.—A study of these spectra from λ2500 to λ7000 at various temperatures of the electric furnace and in the arc and spark has furnished material for a separation of the neutral and ionized spectra, the identification of a large number of neutral lines previously unrecognized, the temperature classification of the neutral spectrum, the selection of ionized lines of lower atomic level, and the identification of new lines, probably doubly-ionized, in the ultra-violet. As in the case of cerium, the neutral lines are brought out much stronger in the furnace than in the arc, and this development takes place within a limited temperature range, indicating in each spectrum a set of low, closely spaced energy levels. In the ultra-violet, the neutral spectrum fades rapidly, and the ionized more slowly, while a rich spectrum appears in the spark, which will probably prove to be that of double ionization. Of these lines, only a few in each spectrum had previously been measured. A notable complexity of line structure was observed in the singly ionized spectrum of praseodymium. Incomplete resolution indicates that with few exceptions each line consists of three to six components, the complexity being more general than in the case of the lanthanum spectrum.

34. Measurement of wave-lengths in the secondary spectrum of hydrogen between 3394A and 8902A. H. G. GALE, G. S. MONK, and K. O. LEE, University of Chicago.—The source was a specially constructed tube, operated by a 1 kw transformer, and cooled with

running water. With a Fabry-Perot interferometer and auxiliary concave grating spectrograph, wave-lengths of 95 strong lines in the secondary spectrum of hydrogen between 4171A and 6527A were measured. For 61 of these lines the probable error is 0.0012A or less; for none of them is it greater than 0.0033A. The spectrum between 3394A and 8902A was then photographed with a 21-ft. focus concave grating in a Rowland mounting, with dispersion of 2.63A per mm and theoretical resolving power of 80,000 in the first order. Wave-lengths of 3064 lines were measured, using the 95 lines measured with the interferometer as standards. Where no such standards existed, the spectrum of iron was used. The mean error of most lines thus measured was less than 0.01A. Many uncertainties in previously published measurements are due to insufficient resolution of close groups of lines. It is believed that the present measures eliminate such uncertainties. Good agreement exists between these measures and those of Merton and Barratt, and Allibone. A systematic difference of 0.24A exists between these measures and those of A. H. Poetker in the extreme red, Poetker's measures being lower.

35. Structure of the OH bands. ROBERT S. MULLIKEN, New York University, Washington Square College.—(Cf. Phys. Rev., **29,** 921; **30,** 387, 785.) Each OH band comprises (*a*) six main branches (*b*) about six weak "satellite" series, (*c*) another weak branch, extending toward high frequencies from each head (λ3064, Watson; λ2811, Jack, Proc. Roy. Soc. 1927). The main branches (for which $\Delta j_k = \Delta j$) and four of the satellite series (for which $\Delta j_k \neq \Delta j$) agree completely with the Hund's case *b* predicted structure for $^2S \rightarrow$ (inverted) ^2P, except that these satellite series, although weak, are much stronger than predicted. Branch (*c*) is now identified as an *R* branch ($\Delta j = 1$,—but $\Delta j_k = 2$); a companion *P* branch, as yet unknown, may be expected. Occurrence of branch (*c*) and high intensity of satellite series show OH here as a transition case between CHλ3900 (good case *b*, six strong branches with $\Delta j = 0, \pm 1$ and $\Delta j_k, = \Delta j$) and HgH (twelve strong branches governed by $\Delta j = 0, \pm 1$ without limitations on Δj_k—j_k not being quantized for the, here case *a*, ^2P state). The ZnH bands lie between OH and HgH in all these features.—Two satellite series (Dieke and Watson's σQ_1 and σQ_2) have $\Delta j_k = \Delta j$ like main branches, but differ by running counter to the usual "crossing-over" rules of σ-type doubling, constituting the first known exception to these rules.

36. Correlation of visible and near infra-red absorption bands in colorless liquids. JOSEPH W. ELLIS, University of California.—Modifying an interpretation previously given (Phys. Rev. **27,** 298 (1926)), it is assumed that an anharmonic series of absorption frequencies originating in oscillations of the carbon-hydrogen bonded pair of atoms starts at 3.2–3.5μ. Data for such series have been compiled from observations with absorption cell thickness varying from 0.01 mm to 2.5 mm, the lowest wave-length members being found in Russell and Lapraik's (J. Chem. Soc. **39,** 168 (1881)) drawings of their visual observations in the visible spectrum. Wave-lengths for typical substances for which the data are most complete are given in microns for (a) benzene; (b) an alkyl derivative of benzene; (c) an amino derivative of benzene; and (d) a halogen derivative of a saturated hydrocarbon.

(a) Benzene:	3.27, 1.68, 1.15, 0.874, 0.713, 0.612, 0.535.
(b) Toluene:	3.38, 1.69, 1.15, 0.876, 0.72, 0.612.
	1.74, 1.18, 0.91, 0.75, 0.637.
(c) Aniline:	3.22, 1.67, 1.14, 0.87, 0.72, 0.612.
(d) Chloroform:	3.32, 1.69, 1.15, 0.88, 0.715, 0.612.

Five of the bands of toluene have now been observed as double, revealing the separate effects of the C_6H_5 (phenyl) and the CH_3 (methyl) types of C-H bonds.

37. The ultra-violet absorption spectra of benzene and toluene in alcoholic solution. C. V. SHAPIRO and R. C. GIBBS, Cornell University.—A study of the absorption spectra of benzene and toluene in alcoholic solution discloses the existence of several heretofore unreported absorption bands. In all 23 bands are found in benzene and 21 in toluene. Many of the new bands are narrow and in general appearance resemble somewhat the absorption bands of the vapors of these substances. Precautions were taken to prevent the presence of vapor between the light source and the slit of the spectrograph. Furthermore a study of the relative position of the vapor and solution bands shows conclusively that none of the absorption bands found in

solution can be ascribed to vapor. With the possible exception of one band belonging to the absorption spectrum of benzene, all of the bands for each substance can be arranged in a series in accordance with a simple mathematical expression derived from the theory of band spectra. Evidence is also presented to show that the recent results reported by Smith, Boord, Adams and Pease, indicating a benzene-like structure for the absorption spectra of a number of organic compounds, were due entirely to the presence of benzene as an impurity.

38. On the mechanism of photo-electric emission. J. H. HSU, Cornell University.—On the assumption that when a quantum of radiation strikes an atom, its energy content is shared by the valence electron and the core of the atom, a simple theory is here described to explain the mechanism of photo-electric emission. According to this theory, the work function $h\nu_0$ should in general be equal to the lowest resonance potential of the substance under investigation. The curve showing the relation between the photo-electric emission and the incident wave-lengths should have humps at certain places. For weak illumination and long wave-length the relationship between photo-electric emission and intensity of incident light should not be linear. Experimental evidences and other phenomena of general interest are brought up and discussed in the light of this theory.

39. The effect of water vapor on the positive air ions. HENRY A. ERIKSON. University of Minnesota.—When initial positive air ions (mobility 1.87 cm/sec per volt/cm) and final positive air ions (mobility 1.36 cm/sec per volt/cm) are passed into air containing water vapor the number of 1.87 ions is at first increased and the number of final ions is diminished. The effect is as if the H_2O molecule gives up an electron to the final positive two-molecule air ion thus neutralizing it and forming in its stead a one-molecule H_2O positive ion. As a 1.87 ion is formed it has not been possible to determine if a similar exchange with the initial (1.87) air ion also takes place. No effect on the negative is observed.

40. The equation of state of a mixture determined from the equations of state of its constituents, and its application in determining the physical and chemical properties of a mixture in terms of those of the constituents. R. D. KLEEMAN, Schenectady, New York.—It is shown that the equation of state of a mixture (whose constituents may be partly or wholly combined into molecules) and the equations of state of the isolated constituents, have the functional forms

$$p=\psi((A_1M_a+B_1M_a+\cdots)/v, (A_2M_a+B_2M_a+\cdots)/v, \cdots),$$
$$p_a=\psi(A_1M_a/v, A_2M_a, \cdots),$$
$$p_b=\psi(B_1M_b/v, B_2M_b/v, \cdots).$$

where M_a, M_b, $\cdots$, denote the masses in gram atoms of the constituents a, b, c, $\cdots$, respectively, p, p_a, p_b, $\cdots$, the pressures of the mixture and isolated constituents, respectively, at the volume v and temperature T, and A_1, A_2, $\cdots$ B_1, B_2, $\cdots$, denote functions of T. The exact form of the function ψ cannot yet be stated; its discovery would be extremely important since empirical forms will not suffice for many purposes. The physico-chemical properties of a substance might thus be deduced from those of the constituents. The equations are shown to form the theoretical basis for expressing the purely physical properties of a complex substance, such as its optical, magnetic, and electrical properties, in terms of the similar properties of the constituents. Such determinations should be possible since a complex substance cannot possess any property the possibility of which did not exist in the isolated constituents.

41. Heisenberg's indetermination principle and the motion of free particles. ARTHUR E. RUARK, Mellon Institute of Industrial Research, University of Pittsburgh, and Gulf Production Companies.—Heisenberg (Zeits. f. Phys. **43,** p. 172) has stated that the error, Δq, committed in measuring a coordinate, and the error Δp, in measuring its conjugate momentum, obey the inequality $\Delta q \cdot \Delta p > h$. At first it seems that an idealized apparatus can be devised to measure the position and momentum of a free particle (having unit mass by definition), so accurately that this inequality is violated. Consider two slits a great distance d apart, which are opened for a short time, one after the other, so that the particle passes both slits; it appears that both

d, and the time in which the particle traverses d, can be measured with great accuracy, so that the velocity is also accurately known. The flaw in this reasoning is the assumption that *either* q *or* p can be measured with any desired accuracy (at least in thought). The measuring devices are statistical aggregates of atoms and are themselves subject to fluctuations. The conclusion is that Heisenberg's principle is valid.

42. On the polarization of light from hydrogen canal rays. F. G. SLACK, Columbia University.—Light emitted at right angles to a stream of hydrogen canal rays is partially polarized. (Electric vector parallel to the beam.) (E. Rupp, Ann. d. Phys. **84**, 94 (1927).) The explanation here offered is based on the theory that an atom excited to a state characterized by a combination of quantum numbers which places the center of gravity of the electronic charge far out from the nucleus favors a transition which results in light polarized with the electric vector parallel to the axis connecting the nucleus with the point of average charge, while an atom excited into the state of the same total quantum number but with a combination of quantum numbers placing the average electronic charge closer to the nucleus (orbits of lesser eccentricity in the Bohr-Sommerfeld theory) favors a transition resulting in light polarized at right angles to this axis. Impacts with the residual gas orient a part of the atoms along the line of the beam in numbers proportional to their respective effective cross-sectional areas. Thus the resultant light is partially polarized with its electric vector parallel to the beam. The computed ratios of parallel intensity to perpendicular intensity are in agreement with the recent experiments.

43. Reflection of atoms at crystal surfaces. A. ELLETT and H. F. OLSON, University of Iowa.—Cadmium and mercury are almost specularly reflected from a *clean* cleavage surface of rock salt. A beam incident at an angle of 45° to the normal to the crystal surface is reflected at 45°, but has its divergence slightly increased. Sodium is not reflected from a rock salt surface, but merely reevaporates if the temperature of the surface is high enough. Atomic hydrogen striking rock salt escapes without being catalyzed to H_2 if the surface is clean. The distribution of the atoms leaving the surface does not indicate either reevaporation or simple specular reflection. The distributon is quite uniform with some crystals, while with others there are quite definite preferred directions. The nearly specular reflection of mercury and cadmium may be interpreted in terms of the de Broglie and Schroedinger ideas, if we assume a discontinuity in the potential energy at the surface of the crystal, but such an interpretation is obviously not necessary.

44. Changes in the electric field due to lightning discharges. J. C. JENSEN, Nebraska Wesleyan University.—Further investigations confirm the general results previously reported, (Bull. Amer. Meteor. Soc., p. 16, Jan., 1925) and are in agreement with the conclusions of Wilson and of Schonland and Craib, that the lower pole of thunderclouds usually carries a negative charge. The totals, without respect to the distance of the storm, now give 635 discharges showing a decrease in a negative potential gradient to 322 showing a decrease in a positive gradient. With storms directly overhead, such ratios as 83:11, 83:19, 42:3 and 82:3 have been obtained. Records of individual discharges have been kept, both, as to their distances and the resulting field changes. When a storm is directly overhead discharges from cloud to earth almost invariably indicate a negative charge on the lower pole of the cloud. Photographs of individual flashes in some cases show a branching towards the earth which is in contradiction to the theory of Simpson. The branches are thin and rambling and suggest the electronic darts mentioned by Dorsey as feeding into the main discharge path.

45. On the determination of the piezo-electric constant of a quartz resonator at high frequency. TADASHI FUJIMOTO, Ohio State University.—A quartz resonator was set oscillating by means of a vacuum tube oscillator. A series of characteristic curves for different values of the impressed voltage was taken and the influence of the number of silver coatings on the displacement number per maximum voltage was studied. The influence of air-gap length upon the voltage required to set the quartz resonator into oscillation was studied and from the curves thus obtained the piezo-electric constant of quartz was obtained.

46. The longitudinal thermomagnetic potential difference in a bismuth crystal. C. W. HEAPS, The Rice Institute.—The longitudinal thermomagnetic potential difference has been measured in plates cut from a single large bismuth crystal. Curves give the results in the form of percent change of thermoelectric power plotted as a function of magnetic field strength. Depending upon relative orientations of crystalline axis, magnetic field, and heat current, a positive or a negative effect can be obtained. The maximum effect observed was a 29 percent decrease in a field of 8000 gausses. It is concluded that the direction of the heat current with respect to the crystal axis or with respect to the magnetic field is of importance in modifying the effect; hence this phenomenon cannot properly be considered as simply an effect of the magnetic field on thermoelectric power, though it is sometimes so considered in the literature of the subject.

47. Factors governing the growth of zinc crystals by the Czochralski-Gomperz method' E. P. T. TYNDALL, University of Iowa.—The production of zinc crystals of any desired orientation has been shown by other workers to be conveniently attained by (1) using as a nucleus a small crystal of the desired orientation, or one so inclined as to simulate this, (2) correct adjustment of the temperature of the molten zinc, (3) correct "rate of drawing" of the crystal. The purpose of the present work is to show that the growth of a zinc crystal of any orientation, started as in (1) above, is (1) independent of the "rate of growth," (2) mainly a function of the temperature gradient existing in the column of liquid zinc between the crystal and the surface of the molten metal. By adjustment of the temperature of the molten zinc and by use of a circular nozzle which directs radial blasts of air, or other gas, at the growing crystal, this temperature gradient may be controlled in a fairly quantitative fashion. It is further shown that crystals of either zero or ninety degree orientation grow with a low gradient, and that the necessary gradient increases for both higher and lower orientations, respectively, reaching a maximum at about forty-five degrees.

48. Magnetic reflection. R. B. ABBOTT, Purdue University.—Experiments suggested by Ross (Proc. A.I.E.E., June, 1920) on "Magnetic Reflection" were carried out on a larger scale. A strong magnetic field was produced by a 500-cycle current passing through a large electromagnet. A large plane coil of wire connected to a resistance coupled amplifier with a telephone receiver, was placed along the axis of the magnet and at some distance from it. The coil was oriented in the magnetic field so that no currents were induced in it. A plane thin sheet of zinc about four square feet in area was then placed at some point in the field and rotated around a vertical axis. As the plate was rotated, a 500-cycle note was produced in the telephone and went through a cycle of intensities corresponding to the angles of the zinc plate. The results show that the zinc plate, due to eddy currents, acted very much like a mirror, the angles of incidence and reflection being about equal. These results were obtained when the zinc plate was twenty feet and more from the magnet and detecting coil.

49. Time lag differences of the Faraday effect in several mixtures and chemical compounds. FRED ALLISON, Alabama Polytechnic Institute.—It has been found that the Faraday effect lags behind the magnetic field longer in one liquid than in another (Beams and Allison, Phys. Rev. **29,** 161 (1927)) and that this lag increases with decreasing wave-length of light (Allison, Phys. Rev. **30,** 66 (1927)). A study of these lags is now in progress with mixtures of these same liquids and also with certain chemical compounds. When two of the liquids are mixed, each liquid retains its own lag, uninfluenced by the presence of the other liquid. The same results were observed for mixtures of several liquids. The compounds thus far studied are acetic acid, several primary alcohols and their acetic acid esters. Lags for various wave-lengths were measured in ethyl alcohol, acetic acid and ethyl acetate. The acetate shows two time lag differences for each wave-length, which are those of the alcohol and the acid. The same results are found for acetic acid, amyl, *n*-butyl and methyl alcohols and the corresponding esters. The lags of the alcohol and the acid are not affected by the chemical union. The ester shows no lag of its own. The method may possibly find an application in detecting the presence of certain constituents of some liquids.

50. A design of x-ray tube for use with vacuum spectrograph or crystal diffraction apparatus. ELMER DERSHEM, University of California.—This tube is almost entirely of metal. The target, filament holder and cathode focusing tube have metal to metal ground cone seals, permitting instant removal for cleaning or for replacement of a burned out filament. Since the target and the cathode focusing tube are very close together (about 3 mm) the limitation of thermionic current by space charge effect is very considerably removed. A saturation current of 140 milliamperes being reached with an alternating e.m.f. of 700 volts and one of 200 milliamperes at 1000 volts. The tube will operate satisfactorily at an impressed e.m.f. of 20 kv even though the air pressure within is above 0.01 mm of mercury.

51. The additive nature of the internal energy and entropy of a substance under certain conditions. R. D. KLEEMAN, Schenectady, New York.—At the previous meeting of the A.A.A.S. the author read a paper in which it was shown that the controllable internal energy and entropy are both zero for a substance or mixture in the condensed state under its vapor pressure at the absolute zero of temperature. The subject has since been further developed to a considerable extent (J. Phys. Chem. **31,** 747 (1927); **31,** 937 (1927); **31,** 1559 (1927). Phil. Mag., **3,** 883 (1927); **4,** 257 (1927); Science, **65,** 210 (1927); **65,** 426 (1927); **66,** 218 (1927)). In the present paper it is shown (from the nature of these quantities without introducing any assumptions) that the internal energies of a number of gaseous non-dissociated compounds of the same type at the same temperature are additive quantities of the atoms, and that this holds also for the differences between the entropy of an arbitrarily selected compound and the entropies of the remaining compounds. These additive laws, for which evidence already exists, will tremendously reduce the labor of determining the foregoing quantities, and the important quantities from the chemists' point of view, the free energies. Furthermore, by considering more data than is necessary an important check on the accuracy of the calculations would be obtained.

52. Infra-red absorption by the N-H bond. JOSEPH W. ELLIS, University of California.—The infra-red absorption spectra of several primary secondary and tertiary aryl, alkyl and aryl alkyl amines have been examined below 3μ with a recording spectrograph. Bands, varying in wave-length between 1.04–1.07μ and 1.49–1.55μ, are found to be present in all of the primary amines and with less intensity in all of the secondary amines. Since they disappear in the spectra of the tertiary amines they are assumed to originate in oscillations of the nitrogen-hydrogen atom pair. The wave-lengths are greatest for the alkyl amines and least for the aryl amines, thus suggesting that the effect of unsaturation in an aryl group is extended to an attached amino group. These two bands, taken with one exhibiting a similar behavior found by Bell (J.A.C.S. **46,** 2192, 3039; **48,** 813, 818; **49,** 1837) at 2.80–3.05μ form an anharmonic series when expressed in frequencies. A band at 0.79μ observed with a 15 cm cell of aniline and one observed visually at 0.650μ by Russell and Lapraik (J. Chem. Soc. **39,** 168 (1881)) in a still longer cell are interpreted as the fourth and fifth members of such a series. Thus there is a similarity in the behavior toward infra-red frequencies between the N-H and the C-H bonds. (See abstract No. 36.)

53. On the collision process accompanying the combination of nitrogen atoms in active nitrogen. BERNARD LEWIS, National Research Fellow, University of Minnesota.—Bonhoeffer and Kaminsky have pointed out that the assumption of a triple collision between two N atoms and a N_2 molecule in active nitrogen resulting in an active unstable molecule, leads to conclusions at variance with certain experimental facts. Another triple collision possibility (forming a metastable excited molecule) is considered and it is shown that unless the relative efficiencies of two competing collision processes change with pressure (considered unlikely), furnishing a possible solution, these results are also contrary to fact. The necessity for a triple collision in the combination of N atoms is therefore discarded. A two body collision between N atoms is next considered, which leads to results in agreement with B. and K.'s observations and also explains other active nitrogen phenomena. Unlike the case of combination of hydrogen atoms, where the intervention of a third body is necessary, the N_2 molecule may be formed in a two-body process since it possesses quantum states, corresponding to the energy of combination plus the relative kinetic energy of the atoms, from which it can radiate.

54. Metallic reflection from rock-salt and sylvite in the Schumann region. A. H. PFUND, Johns Hopkins University.—The regions of anomalous dispersion and metallic reflection in the far ultra-violet have been calculated by others from the known dispersion curves of these substances. These regions have now been found by reflecting, from the above substances, the radiations obtained from a specially designed vacuum tube into a vacuum spectrograph. The maxima of reflection lie near 1600A for rock-salt and near 1625 for sylvite. There are indications of further reflection maxima in the vicinity of 1000A.

55. An approximation method. D. G. BOURGIN, University of Illinois.—A fairly extensive class of problems arising in experimental physics is reducible to the inversion of the integral equation

$$A(x)=\int_{-\infty}^{\infty}(1-e^{-\mu(\nu)x})d\nu$$

Here $A(x)$ is experimentally determined for real, positive x and it is required to characterize $\mu(\nu)$. Two methods of obtaining results are indicated. The first yields an explicit representation of $\nu(\mu)$ in terms of $A(x)$—although mathematically complete it is difficult to apply in practice. The second is empirical and is carried out by choosing a plausible type of $\mu(\nu)$ and determining the parameters by comparison of the calculated $A(x)$ with that given experimentally. The fundamental equation governing this method of approximation is given and an analysis is made of the case that $\mu(\nu)$ is known *a priori* to admit of certain restrictions. A number of theorems correlating the form of $\mu(\nu)$ with the derived $A(x)$ are stated and it is shown that it is therefore possible to determine the nature of the variation in an assumed $\mu(\nu)$ which will improve the approximation. The theorems quoted have special reference to the considerations involved in the study of absorption spectra data of either singlet or doublet lines obtained under conditions of insufficient resolving power.

AUTHOR INDEX

Abbott, R. B.—No. 48
Allison, Fred—Nos. 22 and 49

Baker, Robert H.—No. 5
Becker, Joseph A. and Donald W. Mueller—No. 26
Blake, F. C., James O. Lord, W. C. Phebus and A. E. Focke—No. 15
Bockstahler, Lester I.—No. 10
Bourgin, D. G.—No. 55
Brickwedde, F. G.—see Wait
Brown, S. LeRoy—No. 3

Curtiss, L. F.—No. 4

Davis, Bergen and Harry Purks—No. 18
Davisson, C. and L. H. Germer—No. 24
Dawson, L. H. and W. H. Crew—No. 30
Dershem, Elmer—Nos. 16 and 50

Ellett, A. and H. F. Olson—No. 43
Ellis, Joseph W.—Nos. 36 and 52
Erikson, Henry A.—No. 39

Farnsworth, H. E.—No. 27
Focke, A. E.—see Blake
Friend, F. B.—see Wilkins
Fujimoto, Tadashi—No. 45

Gale, H. G., G. S. Monk and K. O. Lee—No. 34
George, R. H.—No. 8
Germer, L. H.—see Davisson
Gibbs, R. C.—see Shapiro
————, see White
Gibbs, R. C. and H. E. White—No. 32
Gurney, R. W.—No. 23

Hall, E. L.—see Wait
Heaps, C. W.—No. 46
Hsu, J. H.—No. 38

Jensen, J. C.—No. 44

King, Arthur S.—No. 33
Kleeman, R. D.—Nos. 40 and 51
Kunsman, C. H.—No. 25
Kunz, Jakob—No. 20

Lee, K. O.—see Gale
Lewis, Bernard—No. 53
Lindsay, George A.—see Voorhees
Lord, James O.—see Blake

Marcus, Alexander—No. 6
Monk, G. S.—see Gale
Morris, J. C. Jr.—No. 28
Morse, Jared K.—No. 13
Mueller, Donald W.—see Becker
Mulliken, Robert S.—No. 35
Murdock, Carleton C.—No. 12

Nielsen, J. Rud—No. 11

Olson, H. F.—see Ellett

Pfund, A. H.—No. 54
Phebus, W. C.—see Blake
Phillips, T. D.—No. 1

Ruark, Arthur E.—No. 41

Shapiro, C. V. and R. C. Gibbs—No. 37
Slack, F. G.—No. 42
Slattery, Mabel K.—see Wick
Stewart, G. W.—No. 17

Tyndall, E. P. T.—No. 47

Van Dyke, K. S.—No. 7
Voorhees, H. R. and George A. Lindsay—No. 19

Wait, G. R., F. G. Brickwedde and E. L. Hall—No. 9
Wei, H. R.—No. 29
White, H. E.—see Gibbs
———— **and R. C. Gibbs**—No. 31
Wick, Frances G. and Mabel K. Slattery—No. 21
Wilkins, T. R. and F. B. Friend—No. 2
Wilson, Thomas A.—No. 14